A Unifying Mechanistic Model of Mild Steel Corrosion in Weak Acid Aqueous Solutions

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Recent advaces in understanding of the mechanism of mild steel corrosion in the presence of carboxylic acids, dissolved carbon dioxide, and hydrogen sulfide has challenged the conventional views of aqueous corrosion in anoxic weak acid solutions. Conventionally, the high corrosivity of such environments was associated with the direct reduction of these weak acids. Within the last few years, experimental and theoretical investigations of the electrochemical behavior of these corrosive environments suggest that the buffering effect arising from the dissociation of weak acids in the vicinity of metal surface is the main cause for the observed high corrosivity. These findings suggest that neither carboxylic acids, nor the dissolved carbon dioxide, nor hydrogen sulfide are themselves corrosive, and that they merely exacerbate an existing acidic corrosion process. In this study, the buffering effect, being an inherent property of any weak acid, is shown to account for all characteristic behaviors observed in cathodic currents, in all of the cases considered. In order to further elucidate this general behavior, a comprehensive mathematical model was developed and used to simulate the behavior of a hypothetical weak acid, as a function of the kinetic and thermodynamic properties of its dissociation reaction. The mechanistic findings in the present study are framed in terms of a generic mechanistic view of corrosion in weak acid solutions. That enables a simple and generic categorization of weak acids based on their pKa values to serve as a basis to assess the detrimental effect of any weak acid on mild steel corrosion in acidic solutions.

Electrochemical Zero-Mode Waveguide Studies of Single Redox Molecules in Nanopore Electrode Arrays

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It is critically important to understand the relationship between functional states of individual redox enzymes and the macroscopically observed phenotype, which results from averaging over all copies of the same enzyme. Optimally, single enzyme molecules would be studied one-molecule-at-a-time and combined to characterize population behavior. However, studying single electron transfer events in biological systems is quite challenging, principally because the generated currents are below, the noise floor of electrical measurements at accessible gain-bandwidth products. However, the Johnson noise floor can be circumvented by converting redox processes to photon emission events, *i.e.* luminescence, thereby converting the measurements into the shot noise limited regime. Fortunately, flavoenzymes, *i.e.* enzymes with a flavin-based cofactor, exhibit electrofluorogenic behavior, in which the oxidized state of the isoalloxazine chromophore in either flavin mononucleotide (FMN) or flavin adenine dinucleotide (FAD) is strongly emissive in the oxidized, but almost completely non-emissive in the reduced state. However, in order to take advantage of this, it is necessary to isolate single enzyme molecules. To address this problem, we have developed a bifunctional nanoelectrochemical-nanophotonic architecture - the electrochemical zero mode waveguide (E-ZMW) - that can couple biological electron transfer reactions to luminescence, making it possible to observe single electron transfer events in redox enzymes.

Although E-ZMWs may be realized as single nanopores, we utilize parallel arrays of cylindrical nanopores containing either 1 or 2 embedded annular nanoband electrodes. These architectures exhibit several advantages, including: (1) the average occupancy of individual pores may be controlled by concentration, (2) the electrodes in each individual pore are connected to those in all the other pores, so they can all be controlled at the same potential, E_{appl}, and (3) the electrochemical behavior is integrated over the entire array. Thus, single molecule spectroscopic and electrochemical data can be acquired simultaneously. We have used these E-ZMW nanopore electrode arrays to demonstrate strongly correlated single molecule population fluctuations both by correlating the electrochemical currents at top and bottom electrodes and by cross-correlating the electrochemical signals with luminescence signals at the bottom electrode, which also serves as the optical cladding layer of the E-ZMW.[1]

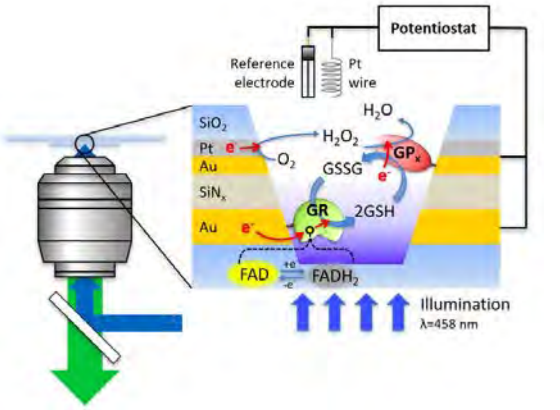

Figure 1. Schematic diagram illustrating the conceptual approach to single electron transfer event observations in the GR-GSSG-GSH system.

Currently, dual-electrode E-ZMWs are being used to carry out single enzyme reduction experiments using the scheme, employing glutathione reductase, GR, as shown in **Figure 1**. The top electrode is used to produce reactive oxygen species in the zeptoliter volume nanopore, for example by the $1e^-$ reduction of O_2 to superoxide, $O_2^{-\bullet}$, which then dismutates into H_2O_2 and O_2. The resulting perturbation of the glutathione redox speciation is then monitored by transients in the single molecule emission of GR.

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From Bioelectrochemistry to Bioelectronics, Biocomputing and “Smart” Materials

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The original goal of bioelectrochemistry has been in the fundamental study of biomolecules, particularly enzymes, communicating with electrically conducting/semiconducting interfaces (electrodes and semiconducting devices). Following the impressive achievements in bioelectrochemistry, especially in mediated and direct electron transfer between proteins/enzymes and electrodes, numerous bioelectrochemical systems have been designed resulting in various biosensors and biofuel cells. Later, more sophisticated systems have been approached, resulting in implantable and wearable bioelectronic devices for sensing and power generation. Novel research directions have been formulated including bioelectrochemical information processing (biocomputing) systems, signal-triggered bioelectrochemical systems, “smart” bioelectrochemical interfaces switchable/tunable by various external signals and capable of electronically stimulated biomolecular release. Studies progressing from conventional electrochemistry to novel multidisciplinary research areas mostly named “bioelectronics” rather than “bioelectrochemistry”, resulted in very impressive scientific results and practical applications. The lecture will briefly address general progress in the research areas of bioelectrochemistry and bioelectronics, concentrating on the author’s personal contribution to the areas. Additional information related to the lecture can be found in the recently published books [1-3].

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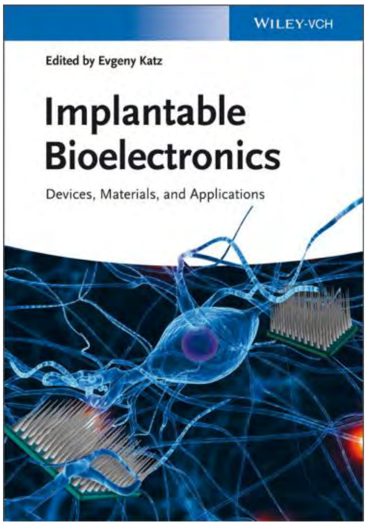

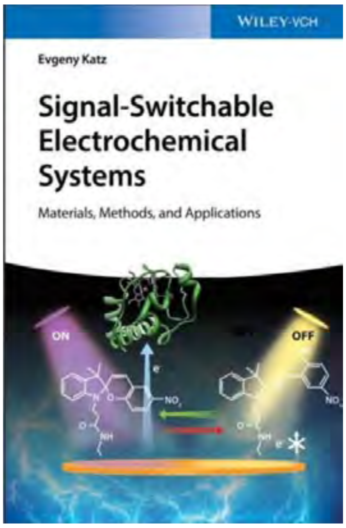

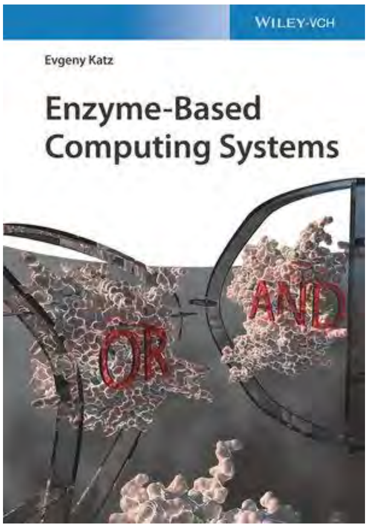

Bioelectrochemical Approaches towards the Detection and Quantification of Drug Resistance in Bacteria and Cancer

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Drug resistance in bacteria and cancer is a growing problem that severely increases the number of deaths from bacterial infections and cancer.[1,2] According to the World Health Organization, drug resistance is present in every country, and various national and international health organizations have called for the urgent development of new treatment and diagnostic strategies.[3] Cellular resistance mechanisms are at the root of drug resistance, which include cell membrane protein modifications, intracellular drug target alterations, and the over expression of efflux pumps.[4]

This presentation outlines innovative and interdisciplinary approaches to recognize and quantify drug resistance in bacteria and cancer cells by electrochemistry. Electroanalytical techniques are cost efficient, sensitive and the transparency of a liquid sample is irrelevant, allowing direct in vitro analysis of blood, urine, and saliva samples. This presentation covers the characterization of some of the most important commercial drugs, and new investigational antibiotic hybrids by electrochemistry.[5] Building on this exploration of drug electrochemistry, the quantification of drug influx and retention in biological cells will be presented. This research forms the basis for the development of a point-of-care biosensor to identify drug resistance in patient samples. Such technology would advance clinical treatment from the current trial-and-error approach to the prescription of evidence-based personalized drug regimens.

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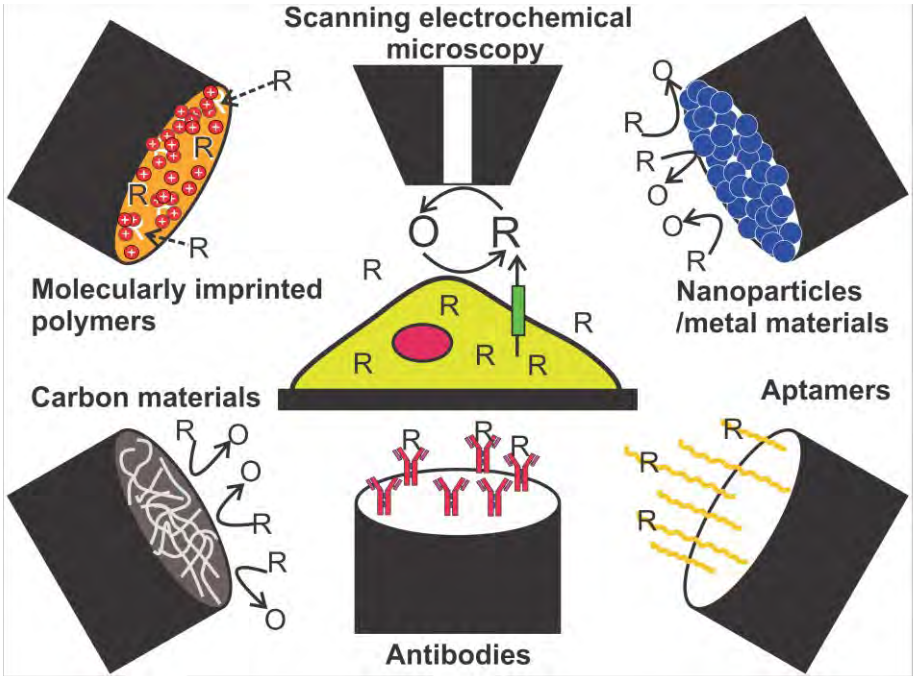

Schematic summary of electrode modification strategies and techniques for the quantitative detection of analytes, such as cell metabolites or drug compounds. R = reduced species; O = oxidized species.

Soft interfaces polarisation: The Helmholtz model strikes back!

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When considering the polarisation of soft interfaces, such as at ion-selective electrode polymer membranes, liquid-liquid interfaces, biological membranes, most textbooks present the polarisation of the interface within the framework of the Gouy-Chapman diffuse layer model.
At a metal-electrolyte interface, the electronic charge distribution is homogeneous at the electrode surface and is described by a homogeneous charge density. On the electrolyte side, the ions compensating the electronic charges are either specifically adsorbed or distributed in what is known as the Gouy-Chapman diffuse layer. Many years of studies at the mercury-electrolyte interface have validated this model.

By extension, the Gouy-Chapman model is used to describe the polarization at liquid-liquid interfaces in what is often referred to as the back-to-back diffuse layers model, where a positively charged diffuse layer in one phase is facing another negatively charged diffuse layer in the adjacent phase. As a result, it is thought that the potential drop between the two phases occurs across a couple of nanometers.

In this talk, we wish to show the limits of this model.

Using different experimental techniques such as impedance measurements, electrocapillary curves, and non-linear spectroscopic techniques together with molecular dynamics simulations, we wish to propose another vision where the polarisation of the interface occurs across a bilayer of interfacial "ion-pairs" (more precisely interacting ions) in what could be called a "discrete Helmholtz" model by reference to the very early work of Helmholtz.

Here, we show that the ion-ion interactions are such that ionic charges do not distribute themselves in a diffuse layer, but by direct formation of interfacial "ion pairs". In this way, all the potential drop occurs across this interfacial ionic bilayer in a stepwise manner. Also, the capacitance of the interface is found to be potential independent for a given "ion pair" and the amount of interfacial "ion pairs" is proportional to the potential difference between the two phases.

We shall illustrate the model to explain the distribution potential of a salt and the electrocapillary phenomena observed with polarised interfaces.

This view of the interfacial polarization of the interface allows us to solve the old dilemma of the potential dependence of electron transfer reactions at liquid-liquid interfaces.

Finally, we shall discuss the extension of the so-called "discrete Helmholtz" model to other interfaces where the charge distribution is not evenly distributed but localized for example in nanostructured solid interfaces as in supercapacitors,

Single-particle microscopy of photoelectrodes

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This presentation will describe our single-molecule fluorescence and photoelectrochemical imaging work on individual semiconductor nanorods under photoelectrochemical water oxidation conditions. I will describe the insights we gained into the charge carrier activities on these semiconductor particle surfaces, how they are related to the photocurrent generation, how deposition of cocatalysts at specific surface sites alters their behaviors, and the efficiency losses from individual particle-particle interfaces.

Reduced Graphene Oxide: Electrochemical Sensing and Therapy

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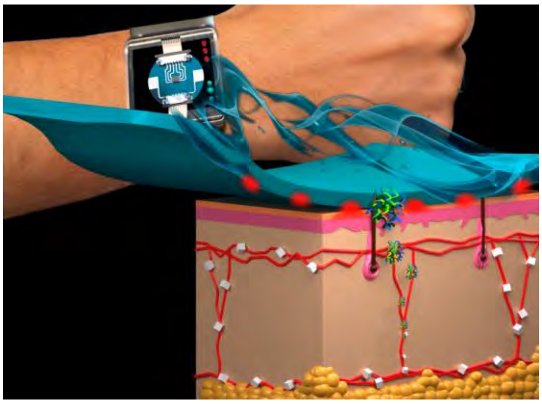
Graphene and its derivatives (graphene oxide, reduced graphene oxide) have drawn tremendous attention from the scientific community as a promising nanomaterial with applications ranging from optoelectronics, high-energy physics, to material science and biomedicine. Different methods have been reported for the preparation of the different graphene-based matrixes. In this presentation, some of your work on the fabrication and interest of reduced graphene oxide (rGO) and rGO-based composite materials for electrochemical sensing and therapeutic applications will be discussed. In the sensing area, the choice of the way graphene is obtained is crucial and will influence strongly electron transfer rates and impact on sensitivity and selectivity to solution analytes. A special focus will be on the use of electrophoretic based approaches for the deposition of rGO and hybrid materials. On the other hand, rGO loaded hydrogels have proven to be versatile controlled-release systems. Some examples on the formation of metformin hydrochloride and insulin loaded bandages for transdermal delivery will be discussed in addition.



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Novel Phosphates and Fluoride-Phosphates Electrode Materials for Me-ion Batteries

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The rapid progress in mass-market applications of metal-ion batteries intensifies the research on electrode materials for Na-ion and K-ion batteries as viable alternatives to the already mature Li-ion technology. Similar to the Li-ion intercalation systems, the Na and K-based mixed oxides and polyanion materials are thoroughly scrutinized as potential cathodes aiming to enhance the specific energy, durability and rate capability. Whereas the layered oxides display greater volumetric energy density, the polyanion materials usually exhibit better cycling and thermal stability and higher C-rate capabilities due to covalently bonded structural frameworks. At the same time compared to the oxide structures based on a close-packed arrangement of oxygen atoms, the polyanion compounds reveal an extra dimension in their crystal chemistry, which significantly extends the playground for designing materials with superior electrochemical performance. Further advantages are expected from the synergistic effect of combining different anions (such as $(XO_4)^{p-}$ and F^-) in the anion sublattice.

An overview of the research on novel transition metal phosphates, pyrophosphates, and fluoride-phosphates as prospective electrode materials for the Na-ion and K-ion batteries will be presented with a special emphasis on the interrelation between chemical composition, synthesis conditions, crystal structure peculiarities and electrochemical properties of the materials intended for practical applications.

Acknowledgements

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Nucleic acid hybridization-induced electrically reconfigurable network of gold-coated magnetic nanoparticles enables ultrasensitive microRNA detection in blood

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The intense interest in quantifying levels of microRNA is because of its importance as a blood-borne biomarker. The challenge has been to develop methods that can monitor microRNA expression both over broad concentration ranges and ultralow amounts directly in a patient's blood. Here, we show using gold-coated magnetic nanoparticles modified by probe DNA (DNA-Au@MNPs) that possess a redox label. The DNA-Au@MNPs diffuse through the sample for analysis and collect the majority of miRNA in a sample before being brought back to the electrode. The resultant microRNA sensor is able to detect concentrations of microRNA from as low as 10 aM to 1 nM in unprocessed blood samples. The exceptionally low detection limits are a result of an unexpected amplification process where hybridisation of a single DNA-microRNA duplex switches off the electrochemistry from hundreds of DNA-Au@MNPs. This amplification system appears to be *via* an electric-field-induced reconfiguration of a network of DNA-Au@MNPs. The highly-sensitive biosensor is capable of direct analysis of nucleic acids in samples as complex as whole blood. It can distinguish small variations in microRNA concentrations in blood samples of animal models that occur due to the presence of a tumour with changes in miRNA levels detected by the biosensor correlated with real-time polymerase chain reaction (qRT-PCR) analysis of the same blood samples. The ultrasensitive and direct detection of microRNA using electrically-reconfigurable DNA-Au@MNPs network makes the reported device a promising tool for cancer diagnostics.

Bipolar Electrochemistry: A Powerful Tool for Organic Redox Reactions

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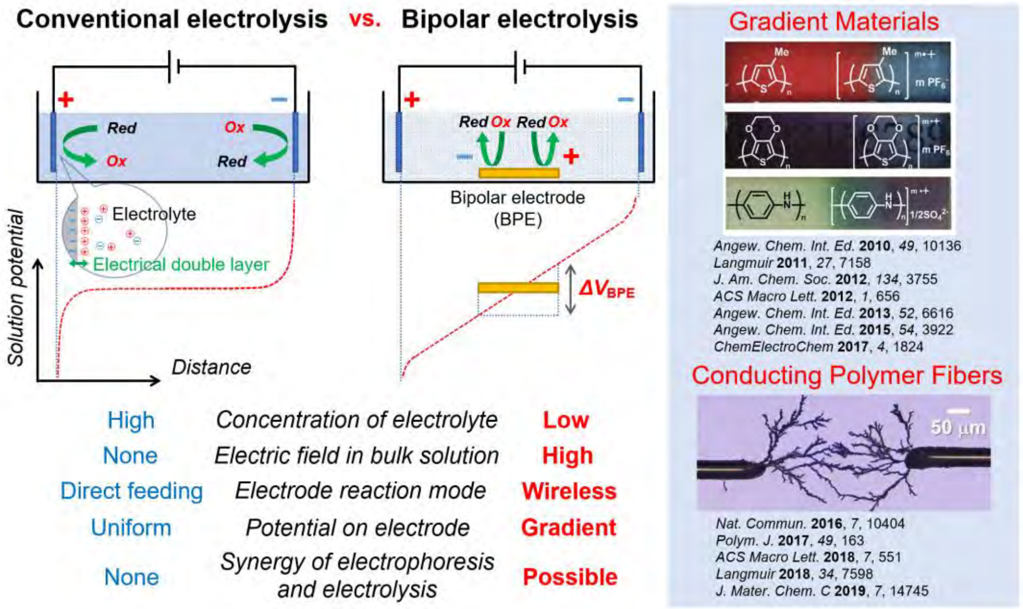
Electrosynthesis is a powerful method for the synthesis of organic, inorganic and polymeric materials based on electron transfer-driven reactions at the substrate/electrode interface. The use of electricity for synthetic reactions without the need for hazardous chemical oxidants and reductants is recognized as a green and sustainable method. A different mode for driving electrochemical reactions has recently been proposed, in which bipolar electrodes (BPEs) are available as wireless electrodes that undergo anodic and cathodic reactions simultaneously. Bipolar electrochemistry is an old technology that has recently attracted attention again due to the interesting features of BPEs because (i) the wireless nature of a BPE is useful for sensors and material synthesis, (ii) the gradient potential distribution on BPEs is a powerful tool for the preparation of gradient surfaces and materials, and (iii) electrophoresis is available for effective electrolysis (Figure 1).[1] In addition to these unique features, a BPE system only requires a small amount of supporting electrolyte in principle, whereas a large amount of electrolyte is necessary in conventional electrochemistry. Hence, bipolar electrochemistry is an inherently green and sustainable chemical process for redox reactions.

In this study, recent progress in bipolar electrochemistry for the electrosynthesis of organic functional materials is summarized. Potential gradients on a BPE interface have been successfully used as controllable templates to form molecular or polymeric gradient materials, which are potentially applicable for high throughput analytical equipment or as biomimetic materials. The wireless nature of BPEs was utilized for symmetry-breaking to produce anisotropic materials based on the site-selective modification of conductive objects by redox reactions including electropolymerization. The electric field necessary to drive BPEs is also potentially useful to induce the directed migration of charged species. The synergetic effects of electrophoresis and electrolysis were also successfully demonstrated to obtain various functional materials. These features of bipolar electrochemistry and the various combinations of techniques have the potential to change the methodologies of material synthesis.



High	Concentration of electrolyte	Low
None	Electric field in bulk solution	High
Direct feeding	Electrode reaction mode	Wireless
Uniform	Potential on electrode	Gradient
None	Synergy of electrophoresis and electrolysis	Possible

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Figure 1. Features and applications of bipolar electrochemistry

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Cyclic Voltammetry: New Theoretical Challenges for Bringing a Famed Electrochemical Lady up to Date

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Cyclic voltammetry has proven its large popularity compared to most other electroanalytical methods owing to its versatility for investigating electrochemical mechanisms and their kinetics. Many textbooks provide clues and laws for understanding and quantifying the main features displayed by a voltammogram. However, this is unfortunately not often useful when confronted to complicated mechanisms as those investigated today. Indeed, most mechanistic situations encountered in molecular electrochemistry at the present time involve complex competitive and entangled reactions that occur indifferently in solutions and onto the surface of electrodes, quite often mixing a series of entwined surface-solution sequences. When confronted to such intricate problems, the classical voltammetric dogma prove helpless and even possibly misleading.

For example, we recently introduced and investigated what is now cited as the "Laviron-Amatore paradox" [1,2] to solve the case of the electrocatalyzed reduction of benzyl chloride at silver cathodes [3]. Although the critical steps were demonstrated to be essentially heterogeneous, involving adsorbed and chemisorbed intermediates, the voltammetric traces displayed none of the expected corresponding features. Conversely, they seemed fully coherent with diffusion/reaction solution processes as if the silver cathodes were playing a strict outer-sphere role. Beyond their favorable catalytic consequences, the same type of essential but hardly detectable surface components present in a mechanism may result in self-inhibitory effects whose drawbacks cannot be rationalized or predicted within classical frameworks [2]. It is presumable that many of such competitive reactions involving exchanges of intermediates between an electrode surface and the solution which feeds the overall process have remained unnoticed due to the lack of dynamic theoretical models and computational approaches prone to detect and apprehend their curious behavior. This is in particular with the objective of allowing the investigations of such finely intertwined heterogeneous and homogeneous steps that we developed our multi-purpose simulation program KISSA$^{©}$ [4].

In this conference, aimed to thank ISE and its Division 6 for the attribution of the Jaroslav Heyrovsky Prize in molecular electrochemistry to one of us, we will present some specific cases of complex voltammetric situations from two first examples studied in the past [5,6].

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How Does a Polycrystalline Electrodeposited Film Grow? Insights from High-Speed AFM

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The problem of how the microstructure and surface topography of a polycrystalline electrodeposited film develop as the film thickness increases is a longstanding one. For example, although ex-situ measurements have shown that both the grain size and the surface roughness of electrodeposited films can increase with film thickness, the details of this process remain unclear[1].

We have used high-speed atomic force microscopy to monitor the surface topography of a Cu film electrodeposited on to a lithographically patterned gold microelectrode from an organic additive-free acid sulfate electrolyte. Measurements are made in real time during growth. The high-speed flexure sample stage of HS-AFM can provide a scan rate 1000 times greater than a conventional AFM, which is key to enabling us to probe much higher deposition rates than previous in-situ studies (currently around 90 nm/s).

The data reveal a number of interesting phenomena. The lateral correlation length appears to increase because different grains grow at different rates. This is accompanied by an increase in local slope, which is also revealed by scaling analysis because surface roughness as a function of deposition time exhibits anomalous scaling[2]. Also, in some cases we clearly observe one grain overgrowing another. A further interesting observation is that, rather than the tip screening the substrate and reducing the deposition rate, tip movement enhanced mass transport significantly during growth: there was accelerated growth where scanning took place compared to other regions of the sample.

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Li-ion batteries: from High Energy to Sustainability

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The announcement of major car manufacturers worldwide to electrify their product line within less than a decade has triggered the large increase of battery cell manufacturing. This will gain even greater momentum once other OEMs will be following this ambition. Lithium-ion batteries are the energy storage technology of choice to enable the deployment of electric vehicles avoiding the use of fossil fuels. However, a transition to a more sustainable production of these cells is required. Consequently, efforts are being invested to develop non-toxic and abundant active materials, for instance, by reducing (if not excluding) the use of cobalt and nickel. Implementing aqueous processing for lithium-ion positive electrodes is another key step towards the achievement of environmentally benign battery production.

Targeting these urgent necessities, we have developed along the years a simple approach leading to the aqueous processing of the high-voltage LiNi0.5Mn1.5O4 (LNMO). This active material is, in fact, considered the most promising for the realization of cobalt-free next generation lithium-ion batteries. First, we demonstrated the feasible use of bio-derived polymers, e.g., sodium carboxymethylcellulose, guar gum and chitosan [1-3], as electrode binders in combination with phosphoric acid, for active material particles and current collector protection, and citric acid, for polymers cross-linking. Thus, to achieve positive electrode tapes readily available for large-scale, high-energy lithium-ion batteries, the use of carbon-coated current collector was introduced, which provides functional groups to crosslink the electrode coating layer to the underlying aluminum foil. The resulting electrodes demonstrate significant improvements concerning the electrode to current collector adhesion and their capacity retention. Through the further optimization of the initial formation cycles, these electrodes offer an electrochemical performance exceeding that of LNMO-based reference electrodes, comprising state-of-the-art poly(vinylidene difluoride) (PVdF) as binder.

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Acknowledgements: This work was funded by the German Federal Ministry of Education and Research within the Li-EcoSafe project (03X4636A & 03X4636D). The financial support of the Helmholtz Association is also acknowledged.instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Catalyst Design and Operando Structure-Composition-Reactivity Correlations during CO_2 Electroreduction

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The utilization of fossil fuels as the main energy source gives rise to serious environmental issues, including global warming caused by the continuously increasing level of atmospheric CO_2. Recently, the electrochemical conversion of CO_2 (CO_2RR) to chemicals and fuels driven by electricity derived from renewable energy has been recognized as a promising strategy towards sustainable energy.

In my talk I will describe the challenges but also provide examples of recent advances in the development of highly active and selective catalysts for the electrochemical reduction of CO_2. The new materials include well-oriented Cu single crystals, plasma-modified nanostructured films, and nanoparticle (NP) electrocatalysts (Cu, Ag, Zn, CuZn and AgSn). Selectivity control in CO_2RR will be achieved through the rational design of the electrocatalyst structure (crystal orientation, atomic arrangement, size, shape, defects), oxidation state and composition. Furthermore, I will also demonstrate how important morphological motives and chemical species can be created and regenerated in pulsed electrolysis experiments.

Finally, the determining role of the electrolyte in the surface restructuring, reaction activity and selectivity will be illustrated. Throughout my talk, the importance of *in situ* and *operando* microscopy and spectroscopy characterization methods to gain in depth understanding on the structure- and electrolyte-sensitivity of real CO_2RR catalysts under working conditions will be highlighted. Our results are expected to open up new routes for the reutilization of CO_2 through its direct selective conversion into higher value products such as ethylene and ethanol.

Towards a Comprehensive Understanding of Platinum-based Electrocatalysis

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Platinum is at the same time one of the most versatile and scarce electrocatalysts. While considerable research efforts have been directed to its replacement in many applications, another plausible strategy is the design of optimal Pt electrocatalysts. In the latter case, the most active sites for each Pt-catalyzed reaction need to be unambiguously determined and fully exploited. A tool for that purpose are "generalized coordination numbers" (GCNs).

In this talk, I will show that GCNs accurately describe adsorption-energy trends for unstrained as well as strained Pt sites on nanoparticles of different shapes and sizes and extended surfaces [1, 2].

Moreover, I will briefly show that "coordination-activity plots" based on GCNs outline the geometric configuration of optimal Pt sites for three important electrocatalytic reactions: O_2 reduction [3, 4], H_2 evolution [5], and CO oxidation [6].

Finally, I will show that GCNs can be used to shed light into two important topics in electrocatalysis, namely adsorbate solvation [7] and the intricate selectivity of organic reactions [8].

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Probing the Solvated Electron at the Electrochemical Interface with a Novel Optoelectronic Method

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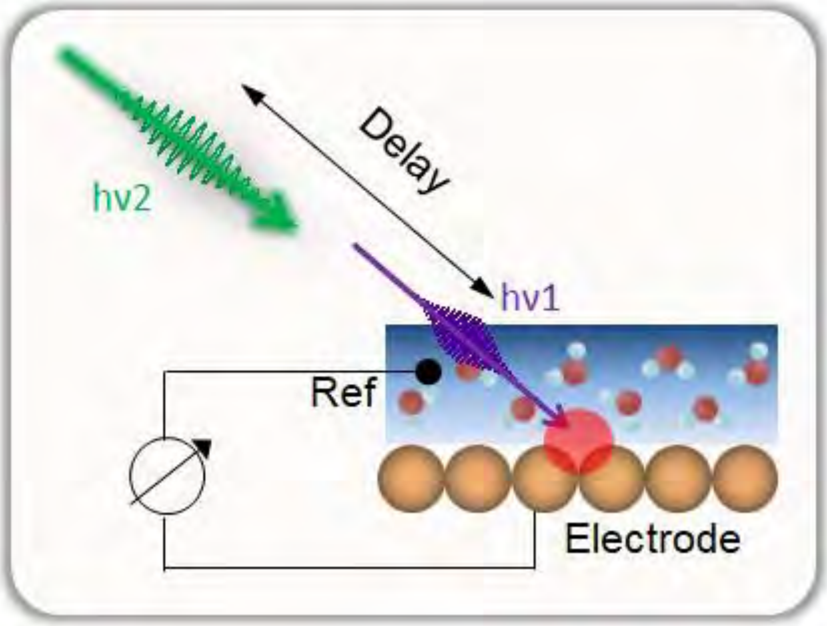
The solvated electron has fundamental and practical significance in radiation and radical chemistry, catalysis and radiobiology. While its bulk properties have been extensively studied, its behavior at electrochemical interfaces is still unclear due to the lack of effective tools to characterize this short-lived species at the condensed matter interfaces. To solve this problem, our group developed a new technology based on ultrashort laser and electrochemical detection (two-photon pump electrochemical probe technique). As shown in in the scheme, here we introduce ultra-short pulse lasers in the traditional electrochemical detection system. One of the lasers is used to excite charge transfer or dipole inversion, and the other laser is used to track the relaxation of the excited state that was trigged by the first laser, while detecting photocurrent or photovoltage in both processes. By adjusting the photon energy of two pulsed lasers and their time difference, we can both obtain the spectral information of the surface species and track ultrafast dynamic processes. In this report, I will use the example of the solvation process of hot electrons at the gold/water interface to show you how this new technique works[1]. This technology will play an important role in the tracking and analysis of various processes in energy and environmental transition in chemistry.



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Atomic Scale Electro-Catalysis

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The chemical industry should in the future be based on renewable energy. Therefore, material development for environmentally friendly, electrocatalytic production of valuable chemicals is needed.

Chemicals could be produced using safe, cheap, more environmentally friendly and more abundant reactants than today. The products could be provided on demand at the place where they are needed, reducing expensive and hazardous transport of chemicals. However, stable, efficient and selective catalysts have to be discovered. This requires insight into the surface chemistry at the atomic scale.

The challenge of discovering new catalyst materials is twofold: Firstly, the properties or descriptors of the wanted catalyst have to be identified. Secondly, real materials with the wanted properties should be found.

I will give examples of determining descriptors for different reactions and a method for identify promising catalyst materials based on high entropy alloy, which is a new class of materials with the promise to change the way we discover interesting catalyst materials.

Electronic Interactions within Mixed Valent Compounds:
- The Influence of Anions, Solvents and Electrostatic Properties -

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The electrochemical properties of bi- and multi-metallic compounds are a convolution of several factors, among which through-bond electron transfer and through-space electrostatic features are the most prominent.[1,2] Besides intrinsic molecular properties, the measurement conditions have a considerable impact on the electronic interactions of mixed valent compounds.[2]

Within this presentation the dependency of inter valence charge transfer (IVCT) on the electrolytes and solvents will be discussed for analytes of different coupling strength. It can be shown that especially for weakly coupled systems the applied measurement conditions have a distinct impact on the energy and shape of the IVCT band while with an increase of the coupling strength the influence of the measurement media diminishes (Figure 1).

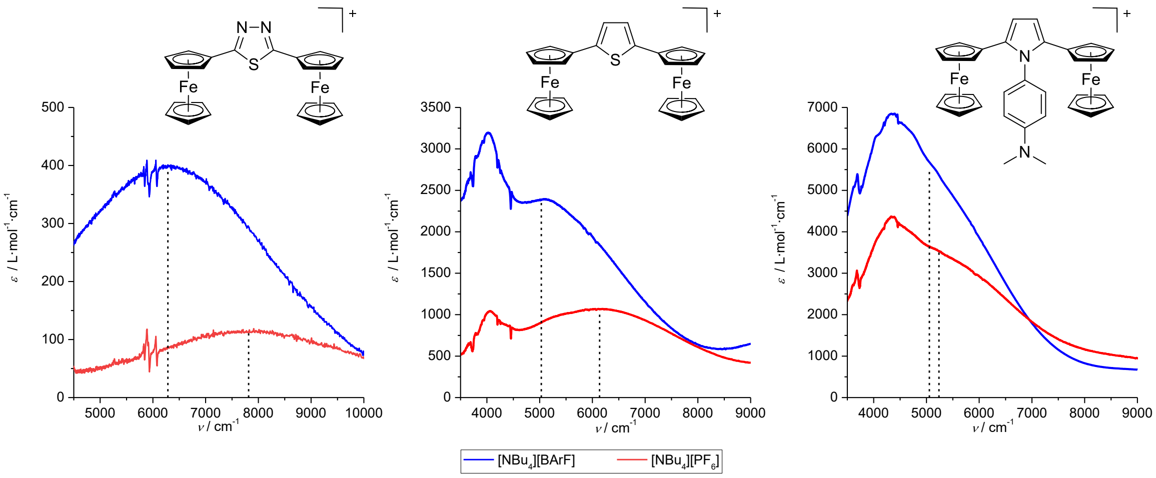

Figure 1. Electrolyte (blue = [NBu4][BArF]; red = [NBu4][PF$_6$]) dependent shift of the IVCT bands of different mixed valent compounds in dichloromethane (BArF$^-$ = B(C$_6$F$_5$)$_4^-$).

In addition, methods that can be used to identify and assess the often less well explored electrostatic contributions to the electrochemical behavior are highlighted. Advances in finding reliable models for intramolecular electrostatic interactions, inter- and intra-molecular influences on the electrostatic properties as well as the exploitation of different ion-pairing capabilities of various electrolytes in order to gain information on electrostatic repulsion energies are discussed.

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Spin-dependent Oxygen Evolution Reaction by Magnetic Oxides

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The oxygen evolution reaction (OER) is the bottleneck that limits the energy efficiency of water-splitting. The process involves four electrons' transfer and the generation of triplet state O_2 from singlet state species (OH- or H_2O). Recently, the OER reactants and products differing in their spin configurations have been thought to cause slow reaction kinetics. Catalysts with magnetically polarized channels could selectively remove electrons with opposite magnetic moment and conserve overall spin during OER, enhancing triplet state oxygen molecule evolution. This talk discuss our recent progress about using ferromagnetic ordered catalysts as the spin polarizer for spin selection under a constant magnetic field to enhance the OER. At the same condition, it does not applicable to non-ferromagnetic catalysts. On the other hand, one example of antiferromagnetic oxides, an inverse spinel structure oxide $LiCoVO_4$, is discussed. It contains d7 Co^{2+} ions that can be stabilized under active octahedral sites, possessing high spin states S=3/2 ($t_{2g}5e_g2$). With high spin configuration, each Co^{2+} ion has an ideal magnetic moment of 3μB, allowing the edge-shared Co^{2+} octahedra in spinel to be magnetically polarized, giving magnetically polarized channels. The average magnetic moment (μ_{ave}) per transition-metal atom in the spin conduction channel is around 2.66μB. Such channels are able to enhance the selective removal of spin-oriented electrons from the reactants during the OER, which facilitates the accumulation of appropriate magnetic moments for triplet oxygen molecule evolution.

Biomolecular Wires of Electric Bacteria: Themes and Variations

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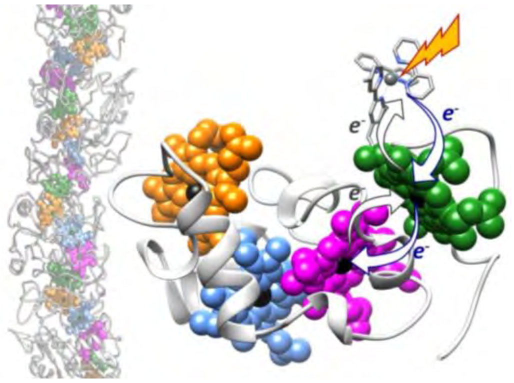
Electric bacteria are naturally able to exchange electrons between internal enzymes and electrodes [1-4]. As a consequence there is much interest in the electrochemistry of these fascinating microorganisms. They can produce clean electricity in microbial fuel cells and value-added chemicals by microbial electrosynthesis. These processes require electron transfer across cell wall lipid bilayers and along extracellular 'nanowire' structures of several microns. Molecular structures of the conductive proteins allowing this electron transfer have recently been revealed for species of *Shewanella* and *Geobacter* [5-7]. The proteins are multiheme cytochromes spanned by chains of close packed heme cofactors. This contribution will review the structures of these proteins and rates of electron transfer across them [e.g. 8-10] to inspire future engineering of such biomolecular wires for disruptive biotechnology operating at both the cellular and single protein levels.



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A Study of Charge Storage in Polyaniline by Electrochemical Means and in situ Electron Spin Resonance Spectroscopy

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Polyaniline is well known for its high reversibility and durability in redox chemistry and related changes in structure, conductivity and chromism. In the past two decades when supercapacitor research has been fast growing, polyaniline, as a model member of the family of conducting polymers, has been widely recognized as a representative of pseudocapacitance [1-4]. During the Covid-19 pandemic lockdown period, the author has paid a re-visit to his own past work that has collected results from experimental and theoretical analyses of electrochemically grown polyaniline coatings [5-7]. Of particular interest to the ongoing effort to differentiate between electric double layer capacitance and pseudocapacitance [7] is the simultaneously recorded electrochemical and electron spin resonance (ESR) signals. This is because double layer charging does not invoke redox chemistry and hence causes no ESR signal change, but electron transfer reactions associated with pseudocapacitance are more likely to generate or eliminate spins. It was revealed that the ESR spectra of polyaniline depended strongly on the electrode potential as shown in Fig. 1, indicating that charge storage in polyaniline is dominantly undertaken by Faradaic processes. It was also confirmed that "surface confined" and "diffusion controlled" charge storage processes can both take place in polyaniline, largely dependent on the conductivity and thickness of the polymer coating. The implication is that although it is highly challenging, if not impossible [1], to differentiate between double layer capacitance and pseudocapacitance by electrochemical means only, it can be realized using in situ spectroscopic techniques.

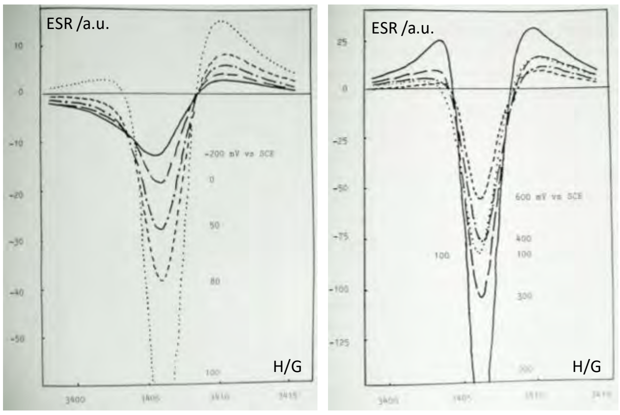

Fig. 1. Electron spin resonance spectra of polyaniline in 1.0 M HCl at the indicated potentials vs. SCE [5].

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Bioelectrical Engineering at the Semiconductor-enabled Biointerfaces

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These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Biointerface devices can probe fundamental biological dynamics and improve the lives of human beings. However, direct application of traditional rigid electronics onto soft tissues or cells can cause signal transduction and biocompatibility issues, due to mechanical mismatch at the biointerfaces. One common mitigation strategy is the use of nanostructures or soft-hard composites to form more biocompatible interfaces with target cells or tissues.

My group integrates nanoscience and soft matter physics with biophysics to study several semiconductor-based biointerfaces. In this talk, I will first pinpoint domains where semiconductor properties can be leveraged for biointerface studies, providing a sample of numbers in semiconductor-based biointerfaces. Next, I will present a few recent studies from our lab and highlight key bioelectrical engineering mechanisms underlying the non-genetic optical modulation interfaces. In particular, I will present a biology-guided two-step design principle for establishing tight intra-, inter-, and extracellular silicon-based bioelectrical interfaces in which silicon and the biological targets have matched mechanical properties and efficient signal transduction. The non-genetic methods have the potential to overcome the limitations of current metal electrode-based devices such as bulk and cell membrane disruption, and are not dependent on genetic modifications. Research in my lab has revealed how the physicochemical outputs from the photothermal, photofaradic, and photocapacitive effects of nanostructured semiconductors can be identified, quantified, and utilized at semiconductor-based biointerfaces to modulate electrical activities in neurons, cardiomyocytes and bacterial cells. Finally, I will discuss new materials and biological targets that could catalyze future advances.

Preparation of Carbon Supported 2D Nanocomposites for Electrochemical Analysis, Biosensing, and Electrocatalysis

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Manufacturing of nanomaterials is an interdisciplinary field covering physics, chemistry, biology, materials science and engineering. The interaction between scientists with different disciplines will undoubtedly lead to the production of novel materials with tailored properties. Binary transition metal oxides (BTMOs) displayed the recognizable benefit in enhancing the sensitivity of analytes detection, these principles preserve all specific properties of both, nanomaterial and biomolecule. Recently, the layered molybdenum selenide with crystal structure has been pointed out as an efficient electrocatalyst for various electrochemical and energy storage applications due to its interesting properties. We have reported transition metals (M = Mn, Ni, Co and Fe) doped $MoSe_2$ and applied as the electrode materials for bio/electrochemical sensors, biofuel cells, and supercapacitors applications. Thus, the utilization of high-quality nanomaterials is now growing and coming to the industrial arena rendering them as the next generation attractive resources with promising applications. Undoubtedly, the existing gap between basic research relating nanomaterials and their application in real life will be overcome in the coming decade. In addition, carbon based materials has been considered as an excellent platform for the preparation of nanocomposite due to its attractive properties including effective surface area, unique structures, mechanical and thermal stability, outstanding charge-transfer characteristics which enhances the electrocatalytic and photocatalytic activity of the supporting material. Moreover, the sulfide functionalities of carbon materials are more responsible for the incorporation of metal molybdates by the electrostatic attraction. Therefore, we are planning to develop an electrochemical sensor based on bimetal sulphides (MxSx, MSx where M =W, Mo, V, Bi, Zn) and sulphides (2D-MS) for the electrochemical detection of various electroactive biomolecules and Supercapactiors applications.

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Operando Surface X-ray Diffraction Studies of Structurally-defined Transition Metal Oxide Electrocatalysts during Oxygen Evolution

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Iron-group oxides are among the best precious-metal-free catalyst for the oxygen evolution reaction (OER) in alkaline media [1] and thus of great interest for large-scale electrochemical water splitting into O_2 and H_2. A wide variety of different catalysts, based on oxides of Co, Fe, and Ni, have been synthesized and studied, exhibiting rather diverse nanoscale morphologies and usually an unknown surface structure. This makes it difficult to compare their reactivity and correlate it with *ab initio* theoretical studies, which hinders the development of clear structure-reactivity relationships and unambiguous determination of the OER reaction mechanism.

In this presentation, approaches for studying structurally well-defined transition metal oxides are discussed. It is shown that the combination of methods for the preparation of oxides with controlled surface orientation with synchrotron-based *in situ* and *operando* surface x-ray diffraction (SXRD) methods can provide detailed insights into these electrode materials under reaction conditions. Specifically, the SXRD techniques allow characterization of the surface and bulk oxide structure over a wide potential range, including the OER regime. These can be performed simultaneously with electro-chemical measurements, enabling direct correlations of structure and reactivity.

As an example, SXRD studies of ultrathin epitaxial films of $Co_3O_4(111)$ and β-CoOOH(001) electro-catalysts [2] are discussed. These two materials show very different behavior. While the CoOOH(001) samples are perfectly stable over a wide potential range, fast and fully reversible structural changes are observed for $Co_3O_4(111)$, in good agreement with a previous study of polycrystalline Co_3O_4 catalysts [3]. Specifically, the near surface region of $Co_3O_4(111)$ is converted to a new phase, which is assigned to highly disordered CoOOH. In addition, continuous changes of the Co_3O_4 unit cell volume are found over a wide potential range, which are assigned to changes in the oxide bulk, related to the pseudo-capacitive charging current in the pre-OER potential range. The kinetics of these structural changes is fast and highly reversible. Despite these differences, the catalytic activity of the skin layer covered $Co_3O_4(111)$ and that of the smooth β-CoOOH(001) are almost identical, if the true microscopic surface area is taken into account. This indicates that the number of OER active sites on the two oxides is similar, despite the very different defect density, and is at variance with previous suggestions that di-μ-oxo bridged Co cations are exclusively responsible for the OER activity of Co oxides.

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Conducting Polymer Biointerfaces

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Conducting polymers (CPs) have been widely used as electroactive biointerfaces in applications such as electrically-stimulated tissue engineering and stretchable organic bioelectronics. In this talk we will present two different approached to electroactive biointerfaces. The first approach overcomes the issue of poor solubility and processability of CP by functionalization of CPs with various moieties, and in particular by grafting of CP backbones with polymeric sidechains. That enables modification of optoelectronic, chemophysical and mechanical properties of the CPs and their use as smart biointerfaces; e.g. responsive to various stimuli, intrinsically stretchable and self-healing. The second approach addresses the issue that electrodes are commonly 2D and as such cannot fully probe the actual 3D cell environment within tissues and organs. Our approach to overcome that is based on a precise fabrication of individually addressable, high aspect ratio, 3D CP-pillar microelectrode arrays by means of 'micro-extrusion printing'. Such 3D microelectrode arrays could be employed in variety of applications, from biological sensing to recording and electrically stimulating cells and tissues, with the design of the arrays being easily adjustable to a particular application.

Electrocatalysis and Bio-electrocatalysis at Nanoscale: The Case for Heterogeneous Catalytic Cascades

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Heterogeneous electrocatalysis in many practical applications is being performed on nano-sized or nano-structured metals and metal alloys. Bioelectrochemistry often studies the charge transfer phenomena in immobilized proteins (enzymes) or enzyme aggregates (quaternary structures), which are also at nanoscale. Currently the most popular enzyme or DNA immobilization platforms and catalyst nano-particle support matrixes are either carbon nanotubes or graphene nano-sheets, both with characteristic dimensions in nanometer range. This implies that if we can master the processes of building the individual catalytic moieties in this scale and integrate also molecular catalysts through the so-called approach of "heterogenization", or tethering the redox catalysts at the interface with a spacer/linker molecule, we can have all those building block arranged, integrated and employed in model catalytic systems performing consecutive (cascade) or parallel reactions "as desired" at the interface. This is the notion of "heterogeneous catalytic cascades" developed by us in a consortium with several collaborators from University of Utah, Columbia, Michigan State University and UC Riverside. All the principals in this collaborative project have discussed the philosophy behind this effort and identified "channeling" as underlying principle for effective multi-step catalysis.[1] Our group have focused on research aiming the development of materials solutions for catalytic cascades, which would integrate bio-catalysis with molecular and heterogeneous catalytic steps.[2-4]

In this talk we will review the technical approaches developed by aiming to integrate functional catalysts from these three quite distinct and often considered as "irreconcilable" types: enzymes, molecular catalyst and metallic nanoparticles and create a functional and practical materials platform allowing cascade reactions catalyzed by all these different species/moieties. We will present design and synthesis of a hybrid enzyme/metal nanoparticle/atomically dispersed nano-material functional catalyst cascade. We will exemplify this idea with examples of building bio-electrochemical devices, where enzymatic catalysis will be enhanced by the heterogeneous and molecular one, with all catalytic moieties co-present at a single "designer interface" based on graphene-like carbonaceous material. This heterogeneous catalytic cascade system is designed around 2D carbonaceous nanomaterial (graphene-like nano-flakes), displayed as am aggregate of those at meso-scale as spheroidal colloidal object: 3D-graphene nano-sheet (3D-GNS). This material allows ease of integration by printing into a paper-based microfluidic analytical platform designed for a confocal Raman microscope for *in situ* spectro-electrochemical detection of the reactin intermediates and products.[5,6]

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Chiral-Induced Spin Selectivity and its Implications for Spin Chemistry and Asymmetric Electrochemistry

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Essential aspects of the chiral induced spin selectivity (CISS) effect and their implications for spin-controlled chemistry and asymmetric electrochemical reactions will be described. The generation of oxygen through electrolysis will be discussed as an example in which chirality-based spin-filtering and spin selection rules can be used to improve the reaction's efficiency and selectivity. Next the discussion will be shifted to illustrate how the spin selectivity of chiral molecules (CISS properties) allow one to use the electron spin as a chiral bias for inducing asymmetric reactions and promoting enantiospecific processes. Two enantioselective electrochemical reactions that have used polarized electron spins as a chiral reagent; enantioselective electroreduction to resolve an enantiomer from a racemic mixture and an oxidative electropolymerization to generate a chiral polymer from achiral monomers. A complementary approach that has used spin-polarized, but otherwise achiral, molecular films to enantiospecifically associate with one enantiomer from a racemic mixture will also be discussed. Each of these reaction types use magnetized films to generate the spin polarized electrons and the enantiospecificity can be selected by choice of the magnetization direction, North pole versus South pole. Possible paths for future research in this area and its compatibility with existing methods based on chiral electrodes will be presented.

Electrocatalysis in Nanomaterial Modified Electrodes and Application to Electrochemical Sensors

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The procurement of new materials and design of materials surfaces for control and improvement of electrocatalysis is one of the primary goals of modern electrochemistry, with applications in many areas. This lecture will focus on strategies to promote electrocatalytic effects with the objective of increasing the selectivity and sensitivity of modified electrodes for electrochemical sensing. It is equally, if not more, important as increasing signals by enlargement of the active surface area, that can lead to lower detection limits and better long-term stability. This will be illustrated by recent results from two main approaches. The first is the use of carbon nanomaterials, carbon nanotubes or graphene, or gold nanoparticles as modifiers either singly or together to exploit synergistic effects, e.g. [1], and combine this with voltammetric or impedance detection. The second concerns electroactive redox polymers formed as films by controlled potential electropolymerisation on multiwalled carbon nanotubes or on iron oxide nanoparticles. For this purpose, we have explored the use of aqueous solutions, of room temperature ionic liquids and, more recently, of deep eutectic solvents (DES) [2] as media for polymer formation. It has been found that the surface morphology of the polymers prepared in DES, particularly acid-doped ethaline DES, increases the polymer surface uniformity and leads to more robust sensing capabilities, whilst also promoting electrocatalytic effects – better kinetics – in the polymer itself. Characterisation of the modified electrode platforms by voltammetric, electrochemical impedance and surface analysis techniques will be demonstrated. Electrocatalysis will be illustrated with model compounds and also showing how they can be used as successful mediators with fast kinetics in electrochemical sensors and enzyme biosensors, e.g. [3,4].

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Electrostimulation of hyperthermophile Thermotoga neapolitana cultures in a Power-to-gas perspective

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The environmental impact of unsustainable growth has led researchers to increasingly address the technologies able to supply clean energy and to minimize wastes. In this new vision, hydrogen is considered a suitable energy vector for renewable energy sources since its utilization is carbon-free and produces only water as a by-product. Particularly, the emerging Power-to-gas concept addresses great expectancy to bio-hydrogen production and also to innovative electromethanogenesis processes which both could exploit culture or coculture of microorganisms in bioelectrochemical systems [1]. The CO2-rich industrial discharged gases and organic wastes could be switched in values, in this way, contributing to solving emission issues and storing otherwise dispersed energy. Methanogenesis usually occurs in thermophile conditions. Nevertheless, thermophile and hyperthermophilic strains, have seldom been explored within the recent attempts to stimulate the bacteria metabolism for novel biotechnological applications.

Thermotogales are among the most hyperthermophilic organotroph (>80 °C) within the bacterial branch of the phylogenetic tree. This bacteria group includes *Thermotoga neapolitana* (DSM 4359, ATCC 49049), a rod-shaped, gram-negative, non-sporulating bacterium, found in the Solfatara craters of Pozzuoli (the volcanic area close to Napoli, Italy), that can release hydrogen and lactic acid from waste organic matter by anaerobic fermentation in marine water [2].

The capability of *Thermotoga neapolitana* to form biofilm and to interact with a polarized carbon surface is presented here, aiming to study new electrochemical biotechnologies of electromethanogenesis in hyperthermophilic conditions. Different types of polarization were tested: i) potentiostatic, ii) potentiodynamic, and iii) no polarization (Open Circuit Potential) in comparison with Control bioreactors without electrodes. Cultures of *T. neapolitana* fed with 30mM of glucose in bioreactors equipped with carbon cloth electrodes, under CO_2 pressure (capnophilic condition) were tested, at 80°C. Chemical analyses of glucose and of the principal glucose metabolites (hydrogen, acetic and lactic acids) were performed after 1-3 days of testing. Biofilm formation on carbon cloth after under different polarizations was documented by SEM observations.

Results from biofilm and electrostimulation tests indicated that a dynamic polarization is able to tune settlement and detachment processes on the electrodes, modifying the bacteria metabolism of glucose fermentation. The presence of electrodes in the bioreactors and polarization caused temporary bacteria starvation on conductive surfaces, followed by high metabolite production. Cyclic potentiodynamic polarizations of ±0.8V between electrodes, with a scan rate of $0.5 mVs^{-1}$, caused an almost totally starvation of bacteria on carbon cloth. An increased polarization of ±1.2V, caused bacteria detachment from electrodes. Some consideration on the type, mode, and intensity of polarization are discussed, from the perspective of a syntropy of this bacteria strain with methanogens in the perspective of an electromethanogenesis process.

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Study on the Initial Stage of Lithium Electrodeposition in Pyrrolidinium-Based Ionic Liquid Electrolytes

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Lithium metal as one of anode materials of batteries can greatly improve the energy density of the battery because of its highest theoretical specific capacity and lowest electrode potential (vs. SHE) [1,2], and Li electrodeposition and dissolution are most fundamental processes of the batteries during cycling. However, fundamental researches have been rarely reported on the initial stage of Li electrodeposition involving nucleation and growth partially because of the presence of the solid electrolyte interphase (SEI) which impose difficulties for monitoring the underneath deposition process. On the other hand, ionic liquids (ILs) having the characteristics of non-flammability, non-volatility, high ionic conductivity and wide electrochemical window can be used as electrolytes for lithium batteries [3]. Herein, we employ traditional electrochemical techniques to study the formation of SEI and nucleation and growth behavior of lithium on Cu surfaces in pyrrolidinium-based IL electrolytes of mixed $Py_{14}TFSI$ and $Py_{14}FSI$ with different proportion and containing the corresponding lithium salt to understand the roles of the anions.

To reduce the impact of Faradaic currents arising from SEI formation during Li deposition, a stable SEI was formed in advance in the IL mixtures with different anion proportions. Electrochemical impedance measurements, in the same electrolytes for SEI preparation, reveal that the impedances of the SEIs formed are different, and they decrease with increasing FSI^- content. Chronoamperometric measurements were then applied to follow the initial stage of Li electrodeposition. Diffusion controlled nucleation and growth behaviors were observed with reduced overpotential at increasing FSI^- content. Fitting by traditional nucleation model [4], taking into account the residual current from SEI reformation[5], Li nucleation process is found close to 3D progressive, which gradually changes to 3D instantaneous nucleation as overpotential increases. The nucleation density N_0 increases with the increase of the overpotential as well as the FSI^- content, indicating that the SEIs performed in higher content of FSI^- are beneficial to the nucleation and growth of lithium. Our work demonstrates that the Li deposition behavior may be regulated by the FSI^- content to adjust the properties of SEI.

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The Nature and Role of Salt Films in Pits

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A framework for pit stability has been established in a series of recent publications.[1-5] The maximum pit dissolution current density, $i_{\mathrm{diss,max}}$, which depends on temperature and maximum potential at the pit surface in a given pit environment, is proposed and compared with the diffusion current density to determine the conditions for pit stability and salt film formation. For an open pit, the criterion for pit stability is that $i_{\mathrm{diss,max}}$ must be greater than or equal to the critical diffusion current density required for maintaining a critical local environment for active dissolution, $i_{\mathrm{diff,crit}}$. The critical condition of $i_{\mathrm{diss,max}} = i_{\mathrm{diff,crit}}$ is associated with three parameters that must be exceeded for stabilization of an open pit: critical temperature T_{crit}, critical potential E_{crit} and critical pit depth r_{crit}. Analogously, the criterion for salt film formation is that $i_{\mathrm{diss,max}}$ must further exceed the diffusion-limited current density i_{lim}, and three parameters associated with salt film formation are: saturation temperature T_{sat}, saturation potential E_{sat} and saturation pit depth r_{sat}. A salt film is not required for pit stabilization; it is just a consequence of a pit achieving diffusion-controlled growth. The main function of a salt film is to adjust the actual potential at pit surface by regulating its thickness, thus to restrict the anodic dissolution rate of pit surface metal at the value of i_{lim}. The film thickness will respond to any changes in the applied potential, temperature, pit depth, ohmic potential drop in the solution and perforation radius of the pit cover. Downward potential scans from the diffusion-controlled condition were performed on SS316L one-dimensional (1D) artificial pit electrodes in 0.6 M NaCl, and experimental evidence is provided to support the validity of the new framework. Using pits of different depths, the maximum pit dissolution current density, $i_{\mathrm{diss,max}}$, was obtained as a function of maximum pit surface potential, E_{max}, at fixed pit surface metal cation concentration. Charge-transfer-controlled 1D pit growth is a transient state, which will spontaneously transition to diffusion-controlled growth. The salt film formed on a SS304 1D pit surface was preserved by flash freezing and characterized using cryo-based focused ion beam/scanning electron microscopy. The salt film exhibits a porous structure. Ni is co-located with Fe in the salt film, indicating the formation of co-precipitated salt containing Fe^{2+} and Ni^{2+}. A salt film growth model at steady state based on ion transport was proposed in which the salt film grows at the metal/salt film interface, while it dissolves at the salt film/solution interface. The growth rate at metal/salt film interface is determined by pit depth, film porosity and the ion mobility. The metal and chloride ion in the salt film are carried by both migration in channels formed by interconnection of the pores and the outward movement of the salt crystallites from the formation of salt below.

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Novel Strategies to Enhance OER Electrocatalysis in Alkaline Media

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The oxygen evolution reaction (OER) is a key process in the general development of sustainable solar fuels, and essential in the progress/growth of an alternative hydrogen economy. This is a very demanding reaction, since a OER catalysts must be fast and efficient, but also stable and robust to high oxidation potentials, water, oxygen, radicals, acids or bases, etc. Several earth abundant metal oxides have appeared as excellent OER electrocatalysts in alkaline conditions, thanks to the robust stability of metal oxides in high pH.[1] The most common agreement suggests that FeNi oxo-hydroxides are arguably the best OER catalyst at pH > 13,[2] although many other binary and ternary candidates appear close in activity.[3] The complexity of this reaction makes difficult to understand and optimize the performance of these catalysts, with the remaining goal to minimize overpotentials, and to maximize current densities. Indeed, after thousands of experiments with multiple phases, the latest progress reports deal with further nanostructuration and smart processing of the materials to increase active surface area.[4]

In this presentation we will introduce some novel strategies to enhance OER activity in alkaline conditions. On one end, we will demonstrate how the use of magnetic fields may boost the performance of classic magnetic metal oxides.[5] On the other end, we will show how a non-redox doping approach opens alternative (and faster) mechanistic pathways.[6] Both strategies were developed from the combination of experiment and theory, as an example of the powerful contribution that computational chemistry can bring to the field, opening new alternatives difficult to disclose or understand exclusively from experimental data analysis.

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Anodizing of various metallic substrates and alloys over a large potential range

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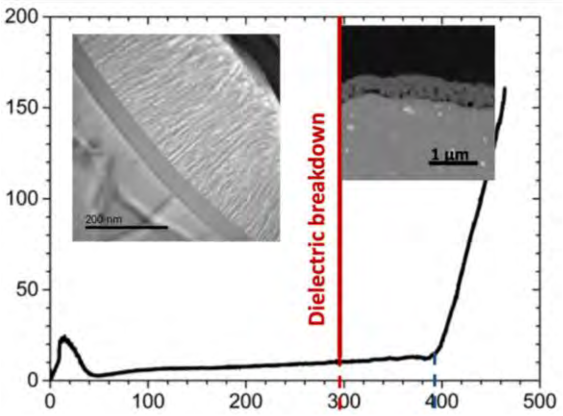
The electrochemical behavior of various metals, namely magnesium, aluminium, titanium and zinc has been investigated over a large potential range.

Whatever the substrate, three successive anodizing steps may be observed:
i) a first "conventional anodizing" step controlled by the solid-state inward migration of O^{2-} and outward migration of M^{n+} ions under the electric field effect,
ii) beyond the dielectric breakdown potential, a range over which the micro-arc phenomenon may occur, leading to the formation of a ceramic like layer,
iii) a "current wall" induced by the increase of oxide conductivity and characterized by a high release of oxygen due to water oxidation.

Electrochemical behavior recorded on aluminium in alkaline medium and typical morphologies of anodic layers relative to different anodizing stages



The possible formation of a ceramic like coating under the effect of micro-arc discharges depends on the physico-chemical and dielectric properties of the inner layer grown by conventional anodizing and governing the occurrence of the dielectric breakdown. The growth mechanisms and the related properties of this inner layer have been finely characterized by combining in situ electrochemical techniques (voltamperometry, in situ electrochemical impedance spectroscopy) and ex situ characterizations of the anodic layers by scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy, X-Ray photoelectron spectroscopy, ellipsometry.

The presence of alloying elements in the substrates may modify the composition and the dielectric properties of the inner layer as well, and consequently the conditions of breakdown occurrence on the one hand and the corrosion resistance of the anodized samples on the other hand.

Through different examples, it has been shown that the chemical composition of the electrolytic solution must be judiciously chosen to ensure an "efficient" growth of the conventional inner anodic layer. Actually, the pH is a key factor to induce an optimal anodic layer growth rate. Moreover, the resistance of the inner layer may be reinforced by the incorporation of additive elements from the electrolyte (silicates, fluorides, etc..). The micro-arc anodizing process may therefore be optimized by lowering the current density necessary to reach the breakdown and the micro-arc regime. The incorporation of additive species in the external porous ceramic layer may furthermore enhance the corrosion performances by acting as sealants during the degradation processes.

In situ studies of the atomic structure/charge distribution at the electrochemical interface

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The presence of specifically adsorbed anions can significantly affect the electrochemical reactivity of a metal electrode which is of major interest for galvanic deposition, etching, corrosion and electrocatalysis. *In-situ* surface x-ray diffraction has enabled an atomic/molecular-level understanding of the interface under reactive conditions, including its potential and time dependence, to be developed. While information about the atomic structure of the electrode surface in electrochemical *in-situ* cells has been widely investigated, insight into the charge distribution and the structure of the electrolyte at the interface is still lacking. Advances in these directions offer possibilities in elucidating atomic scale models of the electrochemical interface and thus will help to establish structure-stability-reactivity relationships.

A fundamental understanding of the nature of the charge transfer, especially the influence of the applied potential and the screening by the electrolyte, is a major goal in electrochemistry to better understand electrochemical processes and charge transfer during adsorption and deposition. [1]

Thus combining x-ray spectroscopy and x-ray diffraction to gain site specific information about the charge distribution at buried interfaces is a promising tool. [2,3]

Examples of how the use of surface x-ray scattering techniques can help to characterise electrochemical interfaces in-situ in order to link, structure, reactivity and stability will be presented. [3,4] Advances in these directions offer possibilities in elucidating atomic scale models of the electrochemical interface and thus will help to establish structure-stability-reactivity relationships.

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Mechanism of boosted electron transfer in microbial electrochemical systems with carbon-based materials

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Electrons can be transferred from electrochemically active bacteria to extracellular electron acceptors with the oxidation of organic matters, which plays important roles in areas of energy production, environmental remediation and geochemical cycle systems. Here we reviewed our latest works about the fundamental research involving extracellular electron transfer (EET) process, and the role of carbon-based materials for boosting EET was also discussed.

Electron transfer process from cell to the electrode: Carbon quantum dots (CDs) could increase the extracellular electron transfer and metabolic rate of *S. oneidensis* MR-1, with increased intracellular charge, higher adenosine triphosphate level, quicker substrate consumption and more abundant extracellular secretion like flavin. Meanwhile, the CDs promoted cellular adhesion, electronegativity, and biofilm formation. In bioelectrical systems the CDs-fed cells increased the maximum current value, 7.34 fold, and power output, 6.46 fold. The enhancement efficacy was found to be strongly dependent on the surface charge of the CDs.

Interspecies electron transfer process: The interspecies electron transfer between *Geobacter* coculture could be promoted by adding biochar as the exogenous mediator. This acceleration process showed a highly positive relationship with the oxygen element content rather than conductivity of biochar.
Multiwalled carbon nanotube (MWCNT) also displayed the acceleration of the electron transfer process in the *Geobacter* cocultures system due to its high conductivity which played a role of electron transfer bridge by connecting cells.

Electron transfer process through biofilm: The electron transfer in a biofilm constructed by mixed cultures could be promoted by inserting MWCNT into the hybrid biofilm. Such a designed biofilm can enhance the EET ability of the biofilm. The specific mechanism analysis showed that the MWCNT insertion can reduce the resistance of the electron transfer through the biofilm. Additionally, it showed a superior selectivity towards exoeletrogens in the biofilm which therefore optimized the community structure.

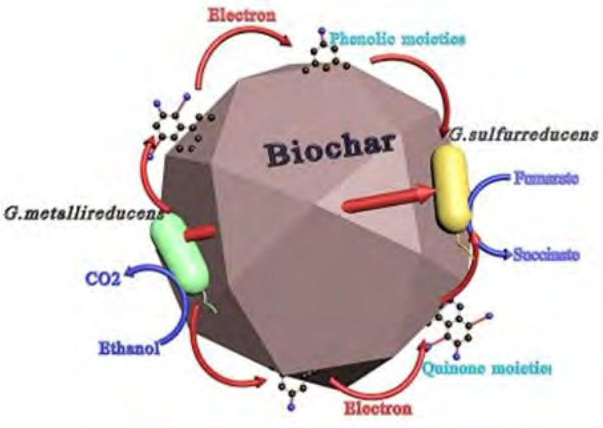

Illustration of the electron transfer process in the microbial electrochemical systems with carbon-based materials

Keywords: mechanism of electron transfer; microbial electrochemical systems; carbon-based materials

Electric Microbes, Metals, and Nanowires

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The Reguera lab investigates electrochemical reactions catalyzed by microbes in natural and anthropogenic systems. Of particular significance is our seminal work investigating how microbes couple their metabolisms via electrical signals and the impact that these activities have in the mineralization of toxic metals and radionuclides. Our interests go beyond the basic research and seek to develop sustainable technologies that harness the electrical activities and conductive cellular components of these organisms in bioremediation and bioenergy applications. In this talk, I will describe novel methodologies we have developed to investigate the physiology of electric microbes and their interactions with biotic and abiotic components of their ecosystem. The basic research provides the fundamental knowledge for applied projects we have developed to harness the power of electric microbes and their components in biotechnology. The translational work also includes collaborations with industrial partners to advance electrochemical technologies for energy and bioremediation applications while providing a training platform for students and postdocs to bridge the great divide between academia and industry.

Pseudocapacitive Effects from Electrolytes and Electrode Materials

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Electrochemical capacitors EC (named also electrical double-layer capacitors or supercapacitors) are the devices based on the reversible storage of energy by electrostatic (capacitive) attraction of ions. Performance of EC are strongly governed by the type of electrolytes, namely aqueous (acidic, basic, neutral), organic and ionic liquids. As a consequence, practical voltage range of EC in these electrolytes varies from 0.8 V to 3.5 V, respectively. The type of current collector will also affect EC voltage values.

Capacitive charge storage can be increased by faradaic reactions, frequently called pseudocapacitive effects. It must be underlined that only redox reactions which present capacitive behavior should be considered, i.e., capacitance should be proportional to the charge accordingly to formula $C = dQ/dE$. Faradaic contribution can be originated from electrode materials but also from electrolytic solutions. Typical electrode materials with pseudocapacitive character consist of: i) electrically conducting polymers, ii) carbon materials rich in heteroatoms (oxygen, nitrogen, sulphur), iii) oxides, e.g., Mn, Ru, iv) carbon with electrosorbed hydrogen. Dichalcogenides such as sulfides, selenides of transition metals (e.g., Mo, Co, V, W) can be used as electrode components to increase capacitance, in turn, energy of supercapacitor.

Exploring redox active species from electrolytic solution is another possibility for energy increase by pseudocapacitive effects [1,2]. Figure 1 shows a big variety of redox couples which could be eventually used for this target. Practical application of such redox pairs will be determined by reversibility, pH of solution, concentration, price, availability, toxic character, influence on capacitor ageing. Some of them can be used only as an additive to electrolyte. Taking into account their potential values, different redox species could serve for positive and negative electrode.

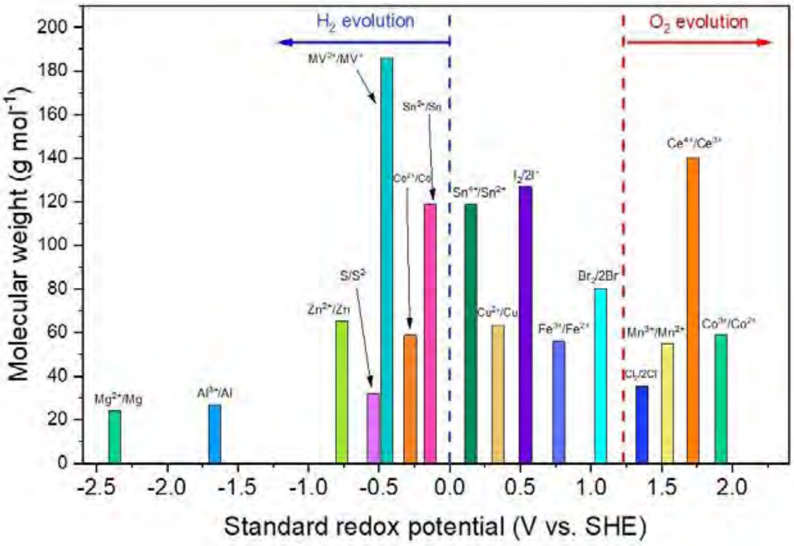

Figure 1: Potential values for various redox couples versus their molecular weight.

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From Inhibitor Screening to Advanced Characterization of Active Protective Coatings

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A cost-efficient and effective corrosion protection measure for metals exposed to corrosive conditions is the application of active protective coatings. These organic coatings provide barrier protection when intact, but also rely on the release of corrosion inhibitors and/or self-healing to protect coating defects upon damage. For decades corrosion inhibitors were based on hexavalent chromium chemistries, but these are now recognized to be extremely toxic and carcinogenic and subject to strict international health and safety legislation.

Many different compounds have been studied to find a non-toxic and environmentally friendly alternative for hexavalent chromium based corrosion inhibitors in active protective coatings by rapid screening techniques and more in-depth mechanistic studies. As an example, over the recent years, lithium-salts have become of interest as a potential alternative for chromates as leaching corrosion inhibitor in organic coatings and demonstrated active protective properties on aerospace aluminium alloys. Further insights into the active protective mechanism of the lithium-based inhibitor coating technology will be presented: leaching kinetics and in-coating inhibitor mobility, formation of a protective layer in a coating defect, the protective mechanism. The results show the mechanistically different behavior of some high-potential inhibitor doped coating technology compared to other inhibitors and demonstrate the key characteristics that are essential for active protective coatings, providing fast leaching, effective inhibition and formation of an irreversible protective layer in the defect area.

Besides inhibitor-based active protective coating concepts also other novel and smart coating technologies based on self-healing of coating defects show a wide variety of promising concepts. With the implementation of a combined polymer and corrosion inhibitor healing concept, the individual and combined time frames for polymer healing and the active surface healing by corrosion inhibitive pigments is even of more importance. Also the analysis of irreversibility of the active protection as well as the time-evolution and duration of protection performance is shown to be of pivotal importance.

This presentation provides an overview of recent advances in the development and characterization of novel inhibitor systems, inhibitor-based and self-healing active protective coatings. Advanced microscopic, spectroscopic and electrochemical techniques will be presented to unravel local corrosion protection mechanisms, inhibitor mobility and leaching from organic coatings as well as inhibitor-based and self-healing coating performance.

Light- versus voltage-driven electron transfer across multi-heme proteins

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Certain bacteria have evolved an astonishing survival mechanisms in response to low oxygen concentrations. When cytoplasmatic oxygen becomes scarce they start to grow µm-long electrically conducting cellular appendages to export electrons from the cytoplasm to extracellular space for reduction of extracellular substrates in place of O_2. Recently it was shown that arrays of Fe-containing multi-heme cytochromes (MHC) confer electric conductivity to those appendages, which garnered much interest for their use in bionanotechnological applications, e.g. bio-compatible field effect transistors. Here I will present recent experimental measurements probing light-driven electron transfer (ET)[1] and voltage-driven electron transport (ETp)[2] through MHCs as well as their interpretation by theory, electronic structure calculations and molecular dynamics simulation[1,2,3]. Specifically, I will discuss recent pump-probe transient absorption spectroscopy results on photo-induced electron injection in Ru-labeled MHCs in solution. We find evidence that the initial ET step along the heme chain occurs via fast, nanosecond heme-to-heme electron hopping[1] in agreement with prior predictions from computations[3]. These results are first experimental evidence for the hypothesis that in biology the micrometer-long electron transport in extracellular respiration occurs via a sequence of many (thousands) of heme-to-heme hopping events. By contrast, we find that voltage-driven ETp in dry MHCs mono-layer junctions is temperature independent and, very surprisingly, best described by coherent tunneling models with tunneling distances of several nanometers spanning the entire protein[2]. The currents across MHCs are orders of magnitude higher (ca 0.1 nA at 0.5 V) than in proteins of similar size (e.g. Azurin) opening up exciting opportunities for the use of MHCs in bioelectronic applications. Taken together, these light and voltage driven studies show that one and the same protein can support different electron flow mechanisms depending on how it is initiated in experiment.

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Ionic Liquids as Co-catalysts for CO_2 Electroreduction in Molecular Electrocatalysis

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Ionic liquids (ILs) in electrocatalysis have attracted a lot of attention from the seminal work of Rosen et al. [1] where they used a mixture with 18 mol% of 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]) in water as a solvent supporting electrolyte system and achieved a relevant overpotential decrease for CO_2 reduction on a silver electrode by forming adducts between CO_2 and reduced imidazolium cations. In fact, it has been demonstrated more recently that imidazolium cations are reduced on the electrode surface as a first step and then form adducts with CO_2, [2-3] which lowers the energy barrier of the unfavorable first one-electron reduction to CO_2. Nevertheless, most of those studies using ILs have been carried out mainly using heterogeneous electrocatalysts. In contrast, much less work has been done exploring the role of ILs in molecular electrocatalysis for CO_2 electroreduction.

The role of different ILs as simultaneous supporting electrolyte and co-catalyst in acetonitrile for CO_2 electroreduction in the presence of a model molecular catalyst [Re(bpy)$(CO)_3$Cl] is presented here. [4] Thus, the structure-activity relationship of ILs on electrocatalytic CO_2 reduction is evaluated by cyclic voltammetry and controlled potential electrolysis. In particular, the nature of the cation, anion and cation alkyl chain is varied by a choice of 5 different ILs, including imidazolium and pyrrolidinium cations and their results are compared to conventional benchmark supporting electrolyte. Under catalytic conditions an overpotential diminution of 0.33 V for CO_2 to CO conversion is achieved in the presence of ILs. Finally, a mechanistic explanation is provided to justify this behavior and the partial suppression of the IL co-catalytic effect when CO_2 electroreduction takes place in the presence of a proton source.

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Beyond Electrochemical ImpedanceSpectroscopy: Advanced Methods forStudying the Dynamics of Electrochemical Processes

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Understanding the dynamic regime of electrochemical processes is of great interest for applications such as water electrolysis for intermediate energy storage of fluctuating renewable energies. Furthermore, dynamic methods are widely used for the diagnosis of electrochemical devices such as fuel cells and batteries and for kinetic mechanism discriminations. In my group different dynamic methods based on periodic changes of electrical [1-4] and non-electrical inputs [5-6] for applications in fuel cells, electroenzymatic systems and kinetic determinations are in current focus.

An example is a so-called non-linear frequency response analysis (NFRA). NFRA can be considered as a generalization of the traditional electrochemical impedance spectroscopy (EIS) where instead of small input amplitudes large input amplitudes are used. This drives the system out of a linear range. Therefore, the nonlinear system response contains a linear contribution which corresponds to the electrochemical admittance, as well as nonlinear contributions. These nonlinear parts of the response give a nonlinear fingerprint of an electrochemical system which can be used for sounder kinetic parameter determination or for discrimination of different rivaling model descriptions. However, the NFRA method is not widely understood and accepted, as it requires fundamental physico-chemical modeling for interpretation and advanced measuring tools. Consequently, research groups that use the NFRA method are very scarce, with no consensus on how the NFR data should be analyzed. In this talk applications of NFRA for kinetic mechanism determinations will be show cased using different examples of simple and multi-step electrochemical reactions [1-4].

In addition to periodic changes of electrical inputs (like current or potential), my group uses also non-electrical inputs to study dynamics of electrochemical systems in a so called concentration-alternating frequency response analysis (cFRA) as a new dynamic method to investigate the dynamics of electrochemical systems [5]. We demonstrated an experimental validation and a measurement routine of this new electrochemical method [6]. In cFRA the electrical response of the cell (current or potential) to periodic perturbation of specific reactant feeds is studied by means of linear system analysis. For the example of a polymer electrolyte fuel cell (PEMFC) we show that cFRA, in contrast to classical electrochemical impedance spectroscopy (EIS), detects selectively the effect of the dynamics of mass transport of reactants and products inside the different layers of the PEMFC. cFRA can also diagnose the humidification state of the fuel cell cathode.

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2D or not 2D: Graphene and related materials in electrochemistry

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In the 12 or so years since the first papers on graphene in the electrochemical context appeared [1], applications of this material in electrochemistry have grown almost unabated. The use of graphene in most electrochemical applications (batteries, supercapacitors, electroanalysis, corrosion protection) has been widely evaluated and electrochemical methods have also been promoted as a route to prepare 2D materials [2]. Two approaches can be discerned in the literature: a "top-down" one, relying on solution exfoliated dispersions, generally of varying thickness and content of oxygen (and other) atoms [3]; and a "bottom-up" one where single flakes, with well-defined properties, are studied [4].

The second approach tends to be guided by advances in sample preparation, where the physics community is now focusing on the "hetero-structures" formed from layers of 2D materials [5]. "Designer" structures can also be performed by assembly of 2D materials with, for example, organic molecules to form assemblies whose bulk properties differ from those of the re-stacked 2D material [6].

A key question for the electrochemical community - which I believe is still largely unanswered - is how the properties of 2D materials – e.g. graphene – evolve as the material thickness increases toward the bulk value (graphite in this case) [7]. Given that graphene is effectively an interfacial film, its behavior (e.g. capacitance, electroactivity with respect to a redox couple, wetting [8]) is strongly affected by the presence of other interfacial films, whether deliberately or accidentally introduced, and by the substrate on which it is supported. Examples of such effects will be presented, along with current thinking about the comparison with graphene and graphite electrochemistry.

2D materials present interesting possibilities to create "membrane" structures, either via random assembly of their flakes [6], via charge transfer through the material (intrinsic [9], or through a drilled hole [10]) or by assembly of nanochannels from these materials [11]. These structures allow unique studies of ion transport, which have only just begun to be exploited in the electrochemical arena.

This lecture will discuss some of the present and likely future directions for this field.

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Electrochemically Gated Charge Transport in Redox Proteins and Photosynthetic Complexes

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Interprotein electron transport (ET) is an essential process in cell respiration and photosynthesis. It takes place between redox proteins and complexes, and it displays an outstanding efficiency and environmental adaptability. Although the biochemistry of ET processes is well characterised, nanoscale experimental methods are needed to understand electronic pathways in these redox protein structures, both for fundamental and for technological purposes. Electrochemical Scanning Tunneling Microscopy (ECSTM) is an excellent tool to study electronic materials and redox molecules including proteins. It offers single molecule resolution and allows working in aqueous solution, in nearly physiological conditions in the case of proteins, and under full electrochemical control. ECSTM also allows performing conductance measurements by current-potential and current-distance tunneling spectroscopy. An overview of these methods and current projects in the laboratory will be presented, with special emphasis on cytochromes of the respiratory chain and on photosystem I complexes.

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Deposition, Wetting and Ion-exchange of Polyaniline and Polyaniline Composite Films in Deep Eutectic Solvents

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Realisation of practical electrochemical devices frequently requires a combination of properties not met by a single component; extension to composite materials is the obvious strategy. Further, electroactive film dynamics - encompassing polymer segmental motion, ion transport and, in certain applications, reactant influx – are dictated by internal electrolyte wetting of the film; the manner in which composite formation influences this is generally unknown. To address these important issues, we explore the relationships between film composition, structure and dynamics as a function of solvent and particulate characteristics for the specific case of polyaniline exposed to a range of protic and aprotic media, from conventional aqueous solutions to deep eutectic solvents.

Commencing from the established baseline of pristine polyaniline deposited from, and redox cycled in, aqueous acid solution, we explore the effect of shifting to the opposite extreme of aprotic ionic liquids (Ethaline and Glyceline) and the intermediate case of a protic ionic liquid (Oxaline). Ion and solvent population changes are determined using acoustic wave measurements (with crystal admittance spectra validating gravimetric responses), as functions of timescale (voltammetric scan rate) and, in selected instances, temperature. Second, we explore the effect of inclusion of physically diverse particulates: multi-walled carbon nanotubes (MWCNT), graphite and molybdenum dioxide; simplistically, these represent geometries of 1D, 2D and 3D inclusions, respectively.

We present the effects of varying solvent characteristics and particulate inclusions on the deposition process and efficiency. For all the combinations (of electrolyte and film components) studied, coulometric and gravimetric assays showed that the films are deposited less than quantitatively, but with acceptable yield. Unsurprisingly, inclusion of particulates influences film morphology. Inclusion of MWCNTs decreases solvation in aqueous medium and in Ethaline shifts maintenance of electroneutrality to cation (choline) transfer, which is reliant upon an adequate internal ionic liquid reservoir, i.e. substantive internal wetting. Multiple redox cycling of Ethaline-deposited films in monomer-free Ethaline drives evolution of film behaviour, but somewhat differently for pristine polymer and MWCNT composite films: pristine polymer is progressively *depleted* of electrolyte, while the composite progressively *accumulates* it. More complex solvation changes accompany medium transfer experiments between aqueous and deep eutectic solvent media, indicative of longer term polymer relaxation processes. These and other effects will be rationalised in terms of the interaction between polymer, the nature of the particulate inclusion and solvent characteristics. The consequences of these outcomes for practical devices will be briefly considered.

Novel highly lipophilic solid contact materials for ion-selective electrodes with reproducible and preadjustable standard potentials

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Ion-selective electrodes are one of the most successful class of chemical sensors that allow separation and sample preparation–free measurements of the activities (concentrations) of a range of essential ions in complex matrices such as whole blood. Even though the potential stability and potential predictability of the conventional liquid contact ion-selective electrodes (ISEs) is hard to surpass, there is a clear trend to replace them with solid contact ISEs. Indeed, the robust miniaturization and mass production of ISEs would largely benefit from a solid contact (SC) configuration. Additionally, ion-selective electrodes emerged most recently as ideal candidates for wearable chemical sensors as they provide a passive transduction mechanism that is not affected by the size of the sensor. However, in case of single use, disposable electrodes it would be desirable if large batches of electrodes with reproducible E^0 and slope could be produced so that the calibration properties of the whole batch could be assessed by calibrating only a limited number of electrodes. Therefore, this aspect gained lately a lot of interest beside ensuring all other criteria for optimal potentiometric behavior of SCISEs.

The two most promising approaches for preparing solid contacts (SCs) for polymeric membrane based ion-selective electrodes (ISEs) are based on the use of large surface areas conducting materials with high capacitance (e. g., various carbon nanotubes) and redox active materials (e. g. conducting polymers). While many of the essential requirements for the potential stability of SCISEs were addressed, the E^0 reproducibility and its predictability, that would enable single use of such electrodes without calibration is still a challenge, i. e., the fabrication of electrodes with sufficiently close E^0 and slope values to enable the characterization of large fabrication batches through the calibration of only a small number of electrodes. The most generic solution seems to be the adjustment of the E^0 potential by polarization prior to the application of the ion-selective membrane. [1]This approach proved to be successful in case of conducting polymer-based solid contacts, and proved to be surprisingly effective also in case of capacitive solid contact based ISEs.[2] Here we are going to report a range of approaches based on chemically modified highly lipophilic carbon nanotubes and similarly lipophilic conducting polymer solid contacts (e.g. perfluorinated alkanoate side chain functionalized poly(3,4-ethylenedioxythiophene)[3] that ultimately led to SCISEs with reproducible potential responses and allowing even for a preadjustment of their E^0 potential.

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Anodic TiO_2 Nanotubes: An Overview

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In the past decade, anodically formed self-organized TiO_2 nanotube layers attracted considerable scientific interest. This is mainly due to the fact that these layers combine the defined nanotubular geometry with a broad range of functional features inherent to TiO_2. Such applications range from solar cells to photocatalysis, over biomedical uses to battery or supercapacitor applications, to support for polymer electrolyte membrane fuel cells.

The presentation will give an overview of the literature available on key features of anodic nanotube layers, as well as critical methods and factors of their formation and most promising properties and applications.

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Perspectives on Organic Electrochemistry – One Persons View

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This lecture will describe a few "perspectives on organic electrochemistry" that the author has developed through decades of experience in the area. Attention will be paid to both synthetic applications as well as mechanistic insights from this laboratory as well as those of other researchers.

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Facetted Nanochemistry of Compounds for Catalysis & Energy

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Systematic computational materials modeling strategies using first-principles methods allow one to describe and understand chemistries of already known materials, and, importantly, they can be used to predict new materials through a careful analysis of the surface chemistry at the atomic level. In this talk, I demonstrate how we have been able to computationally predict several new catalyst materials. I begin by discussing catalysts for electrochemical reactions — the hydrogen evolution reaction (HER) on 2D carbide and nitride materials and the oxygen evolution reaction (OER) on transition metal oxides — that have been experimentally synthesized, characterized and tested. I then share recent theoretical insights on the stability-activity conundrum of oxide materials and present a computationally predicted nanostructured OER catalyst-systems that exhibit a new surface activation phenomenon leveraging our theoretical understanding. I conclude with new efforts to understand more complex nanostructured compound materials' chemistries and geometries used in energy applications beyond catalysis, such as fuel cells and batteries.

Improving the design of electrochemical devices with theory and modelling

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In this talk I will highlight my research on materials and fundamental atomic process that underpin different areas of energy and nanotechnology, such as in electrolysers, batteries and memristors. I will introduce some issues connected with the simulation of electrified interfaces at the nanoscale focusing on modelling the effect of an applied potential to a cell by simulating charged electrodes. I will present some recent progress in our understanding of the interactions of the electrolyte with the metal under applied potential in the technologically relevant Pt-water interface.

Probing the Spatial Heterogeneity of Electrooxidation and the Oxygen Evolution Reaction on Au Operando with Nonlinear Optical Microscopy

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Perhaps the most promising path to the creation of a global energy economy based on the combustion of hydrogen – with its attendant benefits for climate and environmental quality – employs devices based on electrolytic water splitting. Despite much effort, finding relatively inexpensive catalyst materials with high activity and stability has proven challenging. Decades of empirical studies suggest that optimizing the oxidative half reaction, *i.e.* the oxygen evolution reaction (OER), is particularly difficult. Building the best possible devices this underlying chemistry allows requires experimental insight into the *mechanism* of the OER. Gaining such insight requires overcoming at least two hurdles: (a) materials of practical interest are most often heterogeneous over a wide range of length scales and (b) for the most promising metal (oxides) electrodes oxidation of the metal cation occurs at similar potentials to that of the OER. The first limitation implies that a, preferably wide-field, microscopy is required while the second suggests such a microscope should allow *operando* electrode characterization and be capable of imaging both electrooxidation and the formation of molecular oxygen.

In this talk I will discuss our recent efforts to meet these dual challenges through application of the nonlinear optical technique, second harmonic microscopy (SHM), to the operando characterization of electrooxidation and the OER on two different types of structurally heterogeneous Au working electrodes. Because SHM is a background-free probe of surface dielectric function it, allows more precise focusing on the solid/liquid interface and offers a window into surface polarization not available using more conventional optical characterization techniques (with near video rate acquisition). At potentials below the OER and electrooxidation two distinct types of surface optical responses are apparent[1]. More than 80 % of the surface shows a clear positive quadratic response expected from a simple analytic model of electronic polarization of the metal/electrolyte interface. ~ 20 % of the electrode surface area, often near grain boundaries, shows a negative quadratic response with increasing potential consistent with a roughened surface at which anion adsorption occurs at potentials significantly below that of the electrode as a whole. Moving to still more oxidizing potentials we observe the appearance, growth and detachment of individual bubbles[2]. The ability to quantify the flux of O_2 and its spatial distribution makes it straightforward to conclude that the reactivity of the surface with respect to the OER is dominated by < 1 % of the total surface area. These active areas are of two types: presumably deeply penetrating motifs that are stable under potential cycling and more reactive sites that are unstable during surface reconstruction. The later type of active areas are the active sites of Burke et al.'s incipient hydrous oxide/adatom mediator model of electrocatalysis[3].

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Correlative Electrochemical Multi-Microscopy: Towards a Multiscale Understanding of Electrochemical Processes and Interfaces

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Electrodes of practical importance are usually complex on a range of length scales, from the nanoscale to the device level. To address this complexity, we have introduced new approaches, whereby nanoscale information on electrode activity is obtained by electrochemical microscopy in the form of **activity maps** and **activity movies**,[1,2] and these rich datasets are mapped onto **co-located** electrode structure and properties from complementary high-resolution microscopy and spectroscopy techniques. This ***correlative electrochemical multi-microscopy*** strategy helps us to resolve the relationship between local electrode structure and activity. With this detailed microscopic information, an interesting question is can we predict the behaviour of electrodes on larger length scales? More generally, what do we learn about electrochemical systems from a multiscale approach?

This contribution will highlight our recent work using nanoscale scanning electrochemical cell microscopy (SECCM), scanning ion conductance microscopy (SICM) and combined scanning electrochemical microscopy (SECM)-SICM as key techniques for the synchronous acquisition of electrochemical activity-electrode topography,[3,4] coupled with a wide range of microscopy techniques, spanning electron microscopy and electron backscatter diffraction, micro-Raman spectroscopy and atomic force microscopy to pinpoint the nature of particular active sites. With this approach, complex electrode surfaces are studied as set of "single entities" (*e.g.*, individual steps, terraces, defects, crystal facets, grain boundaries, single particles).[1,5] The resulting nanoscale understanding of reactivity is used to create models for electrochemical interfaces and determine how they translate across broader lengthscales and timescales. A wide range of illustrative examples of this general approach will include investigations of 2D materials, single particles and ensembles on electrode supports, and structurally and/or compositionally heterogeneous surfaces, such as polycrystalline metals and polymer composite electrodes. Applications include electrocatalysis, battery electrodes and corrosion. Ultimately, the approaches we advocate provide a roadmap that should facilitate the rational design of functional (electro)materials.

We thank our many collaborators, external to Warwick, who have contributed to our work in this area and will be mentioned throughout this lecture.

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Electrocatalysis on Well-Defined Metal Oxides: Combining Ultrahigh Vacuum Surface Science and Electrochemistry

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Transition metal oxides are promising materials for photoelectrochemical and electrocatalysis. For a molecular-scale understanding of the underlying mechanisms and processes, experiments on well-characterized samples are necessary, i.e., specific facets of single crystals with a known composition, geometry and defect structure. Here the advanced methods of surface science, particularly Scanning Probe Microscopy (SPM) with atomic resolution, Thermally Programmed Desorption (TPD) with accurately-determined coverages, and X-ray Photoelectron Spectroscopy (XPS) with high resolution, together with first-principles computations based on Density Functional Theory (DFT) give unique insights. Bridging the gap to a (photo-) electrochemical environment is challenging, however.

In the talk we will address a first question, namely whether the atomic structure of oxide surfaces – once it is well-established in Ultrahigh Vacuum (UHV) – survives the exposure to liquid water. We use a novel apparatus that allows us to expose UHV-prepared samples to liquid water without exposure to air [1]. We find that the $TiO_2(110)$ surface maintains its (1×1) termination and that a (2×1) superstructure that is typically observed after water exposure in air stems from an ordered layer of carboxylates [2]. In contrast, the $TiO_2(011)$-(2×1) reconstruction is lifted upon exposure to liquid water, and the surface is fully hydroxylated [3]. The $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction [4] of the $Fe_3O_4(001)$ surface is also lifted in water, but the change proceeds slowly together with the growth of an oxy-hydroxide phase with a self-limiting coverage of 0.4 monolayers [5]. By adding CO_2, the pH of the water drop can be adjusted; etching was found to commence below pH~4. Fe_3O_4 was also tested for OER in alkaline conditions, and found to be stable at the nanoscopic scale, with a facet-dependent reactivity [6].

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Interfacing Biocatalysts with Porous Metal Oxide Electrodes for Semi-artificial Photosynthesis

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Semi-artificial photosynthesis interfaces biological catalysts with synthetic materials to overcome limitations in natural and artificial photosynthesis.[1-2] This presentation will summarise my research group's progress in integrating biocatalysts in bespoke hierarchical 3D electrode scaffolds and photoelectrochemical circuits, including the characterisation of the biocatalyst-material interface.[3,4] I will first discuss the fundamental insights gained by integrating isolated enzymes such as the water oxidation enzyme Photosystem II and the CO_2-reducing formate dehydrogenase,[5-11] followed by the more recent exploration of live cells from *Synechocystis* sp. PCC 6803 and *Geobacter sulfurreducens.*[12-14]

The resulting biohybrid electrodes can be explored in the development of novel approaches to solar-to-fuel (and chemical) conversion. For example, the wiring of Photosystem II to a formate dehydrogenase has enabled the *in vitro* re-engineering of natural photosynthetic pathways using semi-artificial Z-scheme architectures.[8,9] In contrast to natural photosynthesis, these hybrid systems allow panchromic light absorption by using complementary biotic and abiotic light absorbers. The underlying photoelectrochemical circuit provides effective electronic communication without losses to competing side-reactions.

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Nanopore Electrochemistry for Single-Molecule Analysis

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Nanopore electrochemistry refers to the promising measurement science based on elaborate pore structures, which offers a well-defined geometric confined space to adopt and characterize single entities including single cells, single particles, and even single molecules by electrochemical technology.[1-3] The electrochemical confined effect within the nanopore displays the incredible ability to achieve single entity discrimination by focusing energy (e.g. electrochemical, light energies and et al.) into small areas, converting the intrinsic properties of single entities into visible electrochemical read-outs with ultra-high temporal-spatial resolution. Furthermore, the excellent resolution of confined nanopore technology also permits the possibility to resolve the transient signals for further revealing the information of single biomolecules dynamics. The chemical controlled confinement inside nanopore provides the advanced electrochemically confined effects to convert the transient single molecule difference into the enhancing signal with high temporal-spatial resolution. In our group, the nanopore electrochemistry has been further applied into disease diagnostics by identifying rare sub-populations, DNA/protein sensing by reading the sequential differences and uncovering the fundamental chemical reactions pathways by revealing the hidden intermediates. With the advents of advanced measurement mechanism, instrumentation and data algorithm, electrochemically confined nanopore is certainly an exciting and promising field. We expect the next avenue for the wide applications of nanopore electrochemistry in a variety of disciplines, leading us explore the new chemistry at a much smaller scale.

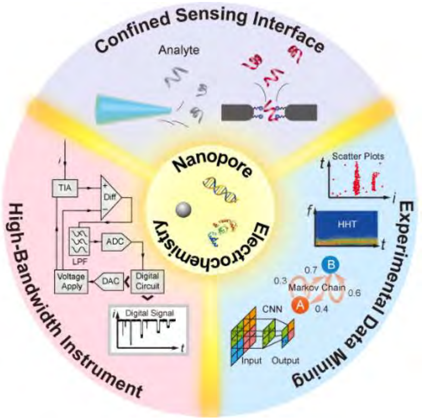

Figure The nanopore electrochemistry for single molecule analysis.

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Insights into the stability and reactivity of solid/liquid interfaces from ab initio calculations

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Processes at solid-liquid interfaces are at the heart of many present day technological challenges related to the improvement of battery materials, electro-catalysis, fuel cells, corrosion and others. Obtaining the microscopic information needed to describe and quantify the underlying fundamental mechanisms is equally challenging to experiment and theory. Density functional theory (DFT) calculations are able to resolve processes at the microscopic scale. However, modelling electrochemical systems is particularly challenging, due to the presence of different classes of materials and phenomena such as metal electrodes, liquid water, huge electric fields within the same system.

Adapting concepts originally developed in the field of semiconductor physics [Phys. Rev. Applied **1**, 014001 (2014)] has enabled us to successfully address questions related to electrochemical processes. This will be demonstrated by two prototypical applications: the selective stabilisation of polar ZnO(0001) surfaces by an aqueous environment [Phys. Rev. Lett. **120**, 066101 (2018)] and the corrosion of Mg surfaces [Phys. Rev. Lett. **120**, 246801 (2018)]. Our development of a novel potentiostat design, which can be easily implemented in all existing periodic DFT codes, allowed us to identify the atomistic mechanism behind the anomalous H_2 evolution reaction on anodically polarized Mg surfaces, which has puzzled electrochemists for more than 150 years.

From Lithium-Rich Cathodes to Solid Electrolyte Interfaces: Atomic-Scale Insights into Battery Materials

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Further breakthroughs in lithium- and sodium-ion batteries require advances in new compositions and underpinning materials science. Indeed, a greater fundamental understanding and insights into these energy-related materials require atomic-scale characterization of their redox, transport and interface behaviour. In this context, combined modelling-experimental work is now a powerful approach for investigating these properties at the atomistic level. This presentation will describe such studies [1-4] in two principal areas: (i) transition metal and oxygen redox chemistry in Li-rich disordered rocksalt cathodes; (ii) ion conduction mechanisms and grain boundary effects in solid electrolytes.

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Iontronics and Reverse Electrodialysis towards Aqueous Circuits

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Ions are charge carriers, which are also main players along with electrons in electrochemistry. Non-faradaic electrochemical systems driven by ion transfer are found in human brains in which neurological circuits exploit difference in electrochemical potential to generate and propagate signals for information processing. Since the new term, *iontronics*, was defined in 2009, ionic circuit for information processing has been increasingly discussed. Starting with ionic diodes, a series of logic gates and even transistors appeared so that aqueous information processor should be on the horizon in terms of the device function as well as material. While the majority of current iontronic systems have relied on electronic power sources like batteries, reverse electrodialysis (RED), an ionic system that produces electricity from salinity gradients, suggests an intriguing settlement of this issue. Recently, RED has evolved not only to increase the maximum power density but also to be miniaturized for applications to various small devices. Highlighting recent advances of iontronics and RED, this talk will discuss the future of combining those two themes.

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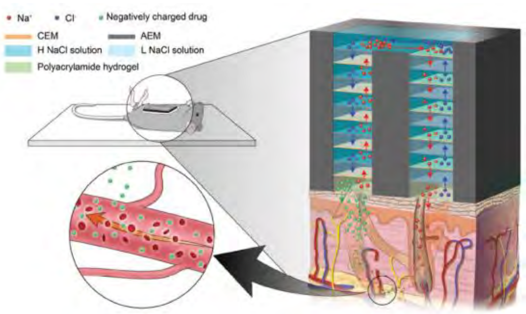

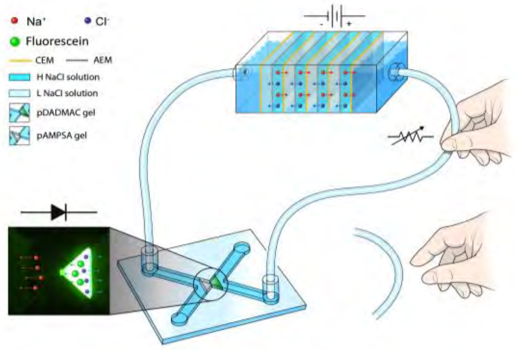

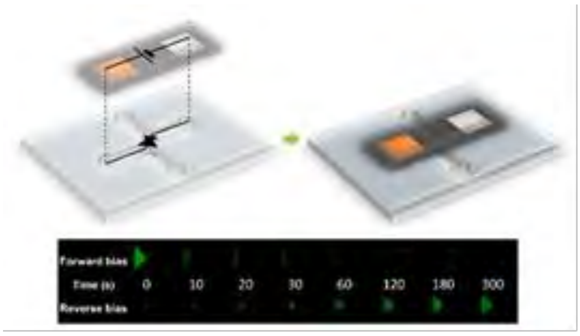

Coupling Electrochemical Detection with DNA Amplification: an Attractive Approach to the Point-of-Care Diagnosis of Virus

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The health threats posed by viral infections such as COVID-19, HIV, hepatitis, influenza, Zika, chikungunya or Ebola, have highlighted the need for rapid, sensitive and selective diagnostic tools to manage the spread of these diseases. In particular, controlling the severe acute respiratory syndrome-related coronavirus-2 pandemic depends critically on the use of genomic diagnostic tests over a large scale. While conventional technologies such as quantitative real-time polymerase chain reaction (real-time PCR) have been broadly used to detect virus (detected through the presence of the viral RNA sequence in a biological fluid), they are expensive, time-consuming, labor-intensive and unavailable in remote settings. Consequently, the development of low-cost and user-friendly point-of-care (POC) viral RNA/DNA testing devices, allowing detection of early infections at limited resource settings or on-field in close proximity to the patient, represent a powerful approach to systematic and decentralized virus detection. To be suitable for limited resource settings, genetic POC devices should ideally be affordable, highly sensitive (the concentration of virus in biological samples can be very low, especially early in the disease cycle, requiring sometime to detect as low as 10^4 RNA copies of viral genome per mL), specific, portable, robust, user-friendly and capable of screening a large number of unprocessed samples in a short time. Toward this end, a major effort has gone into the integration of the gold standard method of nucleic acid analysis, *i.e.* the fluorescence-based real-time PCR, in portable lab-on-chip miniaturized devices. However, to date, real-time PCR has only seen slow transition to POC, in part because of the need for precise thermal cycling, but also because of the requirement for a rather complex, fragile and costly miniaturized fluorescence-based optical detection system. In order to circumvent these limitations, the substitution of PCR by an isothermal DNA amplification, and the replacement of the optical fluorescent read-out by a simpler electrochemical detector, is an attractive solution.[1, 2] Isothermal alternative to PCR have indeed the merit to reduce or eliminate the need for accurate temperature control and cycling, thus affording the development of simpler and smaller battery-operated portable devices. Also important are the numerous advantages offered by an electrochemical detection, namely a lower-cost, a facile integration in a miniaturized format that requires little energy, a good sensitivity, a high robustness without need for periodic recalibration, and the ability to operate in non-transparent reaction mixtures and reaction vessels with complex biological samples. The presentation will be focused on the different approaches we have pioneered and developed,[1-5] including thus the development of a small house-built automatized electrochemical read-out device, optimized for parallel monitoring of up to 48 samples. Some of the recent advances proposed by other groups including chip-based and paper-based POC devices will be also discussed.

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Evolution of Tools in Undergraduate Electrochemistry Education

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The skills and tools of the modern undergraduate differ dramatically from those of generations past. Undergraduates have near instantaneous access to sources of information through electronic devices tied to the Internet. The amount of available information approaches overwhelming. Generations past assimilated scientific content by reliance on more limited information and more sophisticated arithmetic manipulations. Today's undergraduates are facile at retrieving information but perhaps less well schooled algebraically. To help train effective chemical and electrochemical researchers in future generations, educational opportunities must capitalize on the inherent skills of undergraduates and provide tools to organize and manipulate the near unbounded amount of information. Where skills and tools combined effectively, well-educated scientists will be enabled to tackle important problems in electrochemistry.

A new approach to undergraduate education in electrochemistry has recently been undertaken at the University of Iowa. The basic approach is to design modules that couple undergraduates' skills for facile information retrieval with ubiquitously available spreadsheets to build tools that can be used in the course and applied to research problems after completing their degrees. This approach tracks the rapid evolution of information technologies and capitalizes on the undergraduates' inherent skills.

The current course, Analytical Chemistry I, is taken by upper-level juniors and seniors who are largely majoring in chemistry and engineering. The two main topics for Analytical Chemistry I are equilibria and electrochemistry. Modules for equilibrium are based on the systematic treatment of equilibria. Modules for electrochemistry cover equilibrium measurements, spontaneous redox reactions and titrations, nonspontaneous processes such as electrolysis, and the dynamics of voltammetry. In each component, appreciation of the fundamental processes underlying electrochemical behavior is emphasized. The spreadsheets are a tool but also a vehicle for electrochemical education.

Several spreadsheet modules will be demonstrated.

Potential Axis Tool: A spreadsheet-based tool plots a potential axis. From the potential axis, students interpret spontaneous reactions as well as identify the order in which species are electrolyzed. Potential axis is an equilibrium tool with reference to the Nernst equation.

Redox Titration Tool: Students develop a spreadsheet based on fractional concentrations to model redox titrations. This is also based on an equilibrium model.

Voltammetry Tools: Several spreadsheets are developed to appreciate dynamics in electrochemistry. A spreadsheet that emphasizes the critical ideas of flux, current, gradients, and diffusion is developed in a finite difference format for steady state voltammetry. The spreadsheet is modified to transient measurements for chronoamperometry and linear sweep and cyclic voltammetry. The simulations are not precise but suffice to demonstrate the concepts important in electroanalysis. Spreadsheets map the transition from reversible to quasireversible to irreversible electron transfers. Some simple following reactions are also demonstrated.

In preliminary development of spreadsheets to demonstrate ideas of equilibrium and electrochemistry, student learning was enhanced by these tools. In the current Analytical Chemistry I course, students are allowed access to the tools they have built for exams and homework. They also have a final project to use their newly developed tools to either model a system of interest, create a murder mystery problem, or write next year's final.

Acknowledgments

Development of these modules for undergraduate education is supported by the Carver Curriculum Development Grant from the Roy J. Carver Charitable Trust.

Monitoring plant physiology with organic electrochemical transistors

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Plants are the basis of food, providers of oxygen and regulators of the ecosystem. Plants convert solar energy into chemical energy with the process of photosynthesis where carbon dioxide is converted to sugar molecules. Sugars are not only the energy source in plants but also important signalling molecules, involved in regulation of physiology including stress responses. Currently there are no methods that allow real time monitoring of sugar transport in plants. Sugar detection is based on enzymatic assays, chromatography and/or mass spectrometry; all of these methods require sample collection and preparation. Organic electrochemical transistors (OECTs) are ideal tools for interfacing with organisms, since they can translate complex biological input to an electronic readout signal. OECT sensors can operate in complex media and they can directly detect products from the biological unit. In my group we are developing sugars sensors based on the organic electrochemical transistor for monitoring plant processes in-vitro and in-vivo. In a first example we measure the export of glucose in real time, from isolated chloroplasts, with a temporal resolution of 1min. The OECT based platform is able to distinguish the metabolic phase of the chloroplast prior isolation from the plant. In another example we developed implantable OECT-based sugar sensors for in-vivo, real time monitoring of sugar transport in trees. The OECTs sensors show high device to device reproducibility, stability during the operation in the in-vivo environment and most importantly they do not cause a significant wound response from the plant. The sensors reveal kinetics of sugars transport that were not observed before. Our work establishes the OECT-based sensors as powerful tools for monitoring processes in plants, in real time in in-vivo and in-vitro systems.

Electrodeposition of Platinum Metal Films and Alloys Using Surface Limited Redox Replacement Method

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Electrodeposition methods to create epitaxial Pt films and alloys are attractive routes for the design of nanostructures of various shapes and sizes ideal for many fundamental and practical applications. Surface Limited Redox Replacement (SLRR) method has been one of the most successful approaches developed to date that can produce ultra-thin monolayers of Pt with high control of atomic structure [1]. This method is based on the galvanic replacement of a sacrificial underpotentially deposited (UPD) layer of a less noble metal with a more noble Pt through an irreversible surface-controlled limited redox reaction.

Different experimental configurations for the SLRR deposition developed so far include: 1) electrode immersion and transfer between the two solutions containing the sacrificial UPD metal and the replacement metal; 2) the flow-cell set up where the two solutions are exchanged and 3) the deposition in a one-cell configuration, where the UPD sacrificial layer formation and the galvanic replacement reaction with Pt are conducted in the same cell by optimizing solution composition and the potential control.

In this talk, the SLRR method in 'one cell' configuration used for the growth of Pt epitaxial films, and alloys will be described. Electrochemical and surface characterization studies were used to demonstrate the fabrication of high-quality 2D Pt bimetallic systems with controlled film thickness and surface composition. The nature of UPD sacrificial metal and ions present in the solution affect the quality of epitaxial Pt films structure which was exploited in fundamental studies of structure-electrocatalytic activity correlations [2-4]. Besides Cu UPD and Pb UPD based SLRR growth, we demonstrated that hydrogen UPD could be successfully used for Pt thin films growth [2] as well as Pd. The incorporation of UPD sacrificial layer was exploited in the SLRR approach to control the formation of random alloys. By interrupting the UPD galvanic replacement reaction, we showed that it is possible to have controlled 2D $Pt_x Pb_{1-x}$ alloys formation.[5] The SLRR deposition allowed us to examine changes of the adsorption (H and CO) and catalytic behaviour of Pt-Pb alloys as a function of their composition [5].

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Education at the Crime Scene: Visualisation of Latent Fingerprints using Electrochemical Processes

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A key feature of criminal investigations is establishing identities of suspects, victims and witnesses. The most common physical evidence that accomplishes this is a fingermark, since it is unique to an individual and is time-invariant. Its presence can establish contact between an individual and an object (a weapon or an item of value), or place the individual at a fixed location (a crime scene). Most such marks are *latent* (non-visible) fingermarks, which must be rendered visible by a suitable chemical or physical treatment.

A number of latent fingermark techniques rely on electrochemical deposition processes. Interestingly, both students and practitioners commonly find redox chemistry and electrochemical control of surface processes confusing at a fundamental level and difficult to deliver in a practical context. There is a challenge in motivating practitioners to use these methods and students to engage with the underlying science. However, the visual nature of the outcome and its real-world significance can be a potent educational motivator. This presentation conveys recent activities in these areas involving the deposition of conducting polymers and metals using electrochemical control and redox chemistry; in the latter case, we consider circumstances in which the redox chemistry may take place at a metal surface or in solution

We have recently developed a new approach to the visualisation of latent fingermarks on metal surfaces, relevant to both violent crime (bullet casings, knives) and volume crime (tools, handles at points of entry). Simplistically, the fingerprint residue acts as an insulating mask, such that electrochemical processes can only occur on areas of bare metal surface [1-3], to generate a negative image of the fingerprint. When the deposited reagent is a conducting polymer, its electrochromic properties permit electrochemical optimization of image contrast. Solution redox chemistry can also be used to electro-generate elemental silver or gold particles that deposit selectively on the fingermark residue, to generate a positive image of the fingerprint. We have been studying the underlying fundamentals in the application of this concept to the physical developer (PD) method used on paper (documents, currency) and the multi-metal deposition (MMD) method used on polymer surfaces (drug and explosive wrappings).

This presentation will describe translation of these research topics to the educational arena. The primary focus is development of an undergraduate teaching laboratory experiment for students undertaking a *Chemistry with Forensic Science* degree programme. Inclusion of material science, spectroscopic and imaging techniques has the educational benefit of demonstrating the inter-disciplinarity of contemporary scientific research. Educationally, the experiment offers an opportunity to discuss fundamental electrochemical concepts, including electron transfer, coupled chemical (EC-type) processes (proton transfers [1]), electrodeposition, nucleation and growth, redox-driven ion-exchange, and the development of a band structure (in a growing polymer) from the molecular orbital structure (in the monomer). Distinction between thermodynamic and kinetic electrochemical aspects can also be addressed.

The experimental activity can be adjusted to suit students studying at different levels or with diverse backgrounds. It can be delivered in a closed manner based on proscriptive instructions, or it can be extended in various technical directions, incorporating spectroscopic/imaging techniques. Students can also contribute to the experimental design, by selection of appropriate materials or by exploring more applied aspects such as exposure of the "exhibits" to different environments that mimic a crime scene.

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Teaching Translational Research in Electrochemistry: From Fundamental to Product

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Electrochemistry is a discipline of science and technology connecting electron transfer reactions with electrical input and output through electrodes. Therefore, electrochemistry has a fundamentally multidisciplinary nature, which relates chemistry, chemical engineering, material science, process engineering, electronics, and electrical engineering. The key element in electrochemistry is the electrode where electrochemical reaction, reduction, or oxidation, occurs. The charge separation, followed by the electrochemical reactions at the interface, is a fundamental phenomenon in material/energy conversion and mass/ion transport. The understanding of electrode materials and electrochemical processes is the most important in developing the devices and the processes in the fields of energy conversion, power sources, environmental processes, medical devices, and sensors. Therefore, electrochemistry is inherently translational research, which connects the fundamentals of electrochemical phenomena and the applications in developing devices and processes. In this education lecture, I'll use two examples of translationals research, which are currently under development in my lab. 1) CO_2-to-formate or formic acid process is one of the actively pursuing CCU (carbon dioxide utilization) technologies. We succeeded in producing formate to 1.2 M concentration in 30 hrs with the current efficiency of 80~90% at 100 mA/cm^2. The continuous electrolysis could be operated for more than a month. The developed process was applied to build a pilot system of 500 kg/day conversion unit in Hadong power plant, Korea, in 2019. 2) Electroosmosis is a phenomenon in which the fluid moves upon applying an electric field through a capillary or a porous ceramic membrane. This is a rare example where electrochemistry is utilized for a mechanical transducer. Electroosmotic pumps are the simplest one, consisting of two electrodes separated by a porous membrane. We developed a non-gassing electroosmotic pump, in which the traditional platinum electrode is not in use, and made the pump system stable and efficient. It also enabled the pump battery-operable. The pump is currently being used to develop drug pumps such as an insulin patch pump and an implantable morphine pump.

Activity of electrocatalysts. From common wording to common pitfalls

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Activity of an electrocatalyst is an intrinsic property which essentially is related to the turnover frequency of an active site exposed at the surface of a catalyst modified electrode to the electrolyte and can be expressed as the current per active site at a given overpotential with respect to the thermodynamic value. Evidently, common laboratory praxis is to integrate powder-based electrocatalysts into an ink together with a binder material (often Nafion) and/or conducting additives (typically carbon materials), to drop-coat a rotating disk electrode or the disk of a rotating ring/disk electrode and to investigate linear sweep voltammograms at a typically not too fast scan rate. Normalization is then often performed by dividing through the footprint of the electrode surface. This leads to a current density value at a chosen overpotential which is then used to compare different catalyst activities.

As a matter of fact, this is by far too simple to describe and even more to compare catalyst materials and later use the words “better” or “best” for the candidate with the highest value for a given reaction.

In this presentation the aim is to alert for the use of words like “onset potential”, consideration of how to calculate the potential against the reversible hydrogen electrode, the complex impact of catalyst film thickness, inter-particle conductivity, local pH values, ion movement, the role of the double layer, the presence of porous materials on the response in a simple linear sweep voltammograms.

Furthermore, it will be described why using single entity electrochemistry by application of nanoelectrochemical tools are contributing to an improved understanding of the processes ultimately govern the complex current response during electrocatalysis.

Acknowledgements:

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Teaching electrochemistry with youtube.
Something new under the sun?

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Electrochemistry is an experimental science with beautiful visual phenomema. There are many ways to teach electrochemistry, its methods, concepts, theories, models, laws, reactions, mechanisms, etc. The teaching may be based on historical or phenomenological approaches. It can also start from the concepts and then move to the applications. Whatever the selected approach is, it depends on the teacher, its pedagogical goals and of course the audience, in other words, the students.

Most of our present and future students belongs to the generation Z (the next one is the generation Alpha). This generation has never known a world without computers and cell phones. In fact, most of them integrated completely the multimedia technology, internet and the social networking sites (Facebook, MySpace, Twitter, LinkedIn, etc.). The way they learned by sitting at a desk with a book, notebook and pencil is changing. Textbooks and notebooks are being replaced with tablets and the pencil by the stylus. Touchscreen technology and cloud computing are transforming how, where, and even when students learn. They are much more stimulated by the visual impact of images and videos. Therefore, the teachers have to adapt to these new students.

In this talk, we will present a few examples based on videos mainly from youtube to teach electrochemistry.

Education, a vehicle of transformation.

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Historically education was based on knowledge as a transformation tool from poverty to wealth as humanity dealt with inequalities brought about by colonialism, racism, geographic disparity and many other obstacles. Education was the key, the wealth and the new bartering currency as society transformed itself. The first industrial revolution brought industrialization and urbanisation to agriculture. This was closely followed by a second transformation wave, with advances in steel production, electricity and petroleum, leading to a series of innovations that changed society. The third industrial revolution saw a rise of electronics, telecommunications and of course computers, opening the doors to space expeditions, research, and biotechnology.

For society to benefit fully from its investment in science education, knowledge must be accessible and familiar to a global community of users who have the skills, knowledge and understanding to unpack and apply learning to societal challenges (1). Scientists need to draw on multiple data and information sources, data analysis skills, statistics and models to create knowledge that is communicated effectively to decision-makers in government, industry, and civil society.

The World Economic Forum (WEF) estimates that 65% of children entering primary schools today will end up working in entirely new occupations or jobs that do not exist now. Therefore the fourth industrial revolution appears threatening to many. It is perceived to be a threat to job security as well as the ordinary way of doing things (2). The various technologies that power the 4IR concept include, artificial intelligence and robotics; ubiquitous linked sensors; virtual and augmented realities; additive and distributed ledger technology; advanced materials and nanomaterials; energy capture, storage, and transmission; and new computing technologies, biotechnologies, geoengineering technologies, neurotechnology, and space technologies. In this paper we will provide some perspectives on technology as a threat or opportunity, as we move from old into the new, examining relevant weaknesses and strengths of education as a vehicle of transformation.

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The Importance of Practical Elements in Electrochemistry Education

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Drawing on experience from outreach activities, such as the Southampton Electrochemistry Circus, and continuous professional development activities, such as the Southampton Electrochemistry Summer School, I will show how hands-on practical elements help to both inspire the next generation of electrochemists and deepen understanding of the theoretical aspects, respectively.

Electrochemical Biosensors: A good example for teaching at the boarder of disciplines

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Quantification of biological or biochemical processes are of utmost importance for medical, biological and biotechnological applications. However, converting the biological information to an easily processed electronic signal is challenging due to the complexity of connecting an electronic device directly to a biological environment. Electrochemical biosensors provide an attractive means to analyze the content of a biological sample due to the direct conversion of a biological event to an electronic signal.

The signal transduction and the general performance of electrochemical sensors are strongly determined by the surface architecture that connect the sensing element to the biological ligand. Furthermore, the choice of the surface linked receptor as well as of the electrode material used influence the ultimate sensitivity of the biosensor. New nanotechnology-based approaches have become crucial in the development of advanced electrochemical biosensors. Some of these aspects will be presented here to make these aspects more understandable to the young generation of electrochemists interested in this field.

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Effective online teaching in electrochemistry and beyond: teacher and student perspectives

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Chemistry is recognized as one of the most difficult subjects at all levels of education, and electrochemistry is seen as one of the most challenging components of chemistry programmes for teachers and students alike. The worldwide shift to online education in spring 2020 further compounded the difficulties faced by educators in making chemistry accessible to learners and, with the likelihood that campus teaching will be disrupted for some time to come, it is imperative that we enhance our provision of remote learning going forwards.

This presentation considers the findings of research carried out to investigate students' experiences of online learning on a chemistry course at the University of Southampton towards the end of the 2019/20 academic year. The mode of delivery implemented was informed by previous work in the area of flipped teaching[1] and self-assessment activities for students[2]. The findings of the research provide clear guidance regarding effective approaches that others might wish to adopt to ensure student engagement in online learning and maximize student achievement in electrochemistry and other areas of the subject.

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Electrochemistry and Electrochemical Engineering: University of California Irvine comprehensive graduate program at PhD, MS and ME levels

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UCI Electrochemistry & Electrochemical Engineering graduate program initiative was born in a series of ad-hock meetings of groups of UCI faculty members early in the Fall of 2018 with realization of reaching a critical mass in this intrinsically interdisciplinary area of research, two decades of offering a "classic" electrochemistry class in Chemistry (part of School of Physical Sciences), the existence of multiple electrochemistry modules and a set of Fuel Cell Technology classes at the Advaced Power and Energy Program, Samueli School of Engineering. Artur M. Sackler Colloquium of the National Academy of Sciences on *Status and Challenges in Science for Decarbonizing our Energy Landscape* (October 10-12, Beckman Center, Irvine, CA) saw the presence of some 17 UCI professors with a self-declared adherence to electrochemical science and engineering ranging from photo-electrochemistry, bio-electrochemistry, sensors & actuators, high-temperature electro-chemistry and solid-state ionics, electrochemical energy technology and power systems and corrosion. It was this very fact of self-identification that is the most powerful impetus for this initiative to create a graduate program at both PhD and MS/ME levels.[1] It came with the spark realization that at present, in the US, (and could be also in Europe or in Japan), there is no other university campus with such high concentration of achievement and talent in the general area of electrochemistry. It came also with the call from the key constituencies: the high-technology wave of renewable energy integration into the grid, highest demand for electricity storage, new mobility and propulsion and with the need to transform critical chemical processes, like Haber-Bosch ammonia synthesis, or Fischer-Tropsch processing of CO and hydrogen to liquid fuels. Electrochemical sciences will play fundamental role in freeing humanity from dependence on fossil fuels and associated high temperature / high pressure processes. Electrochemical engineering is one of the ways to introduce environmentally friendly, low-temperature, solution-based technologies and is the base of hydrogen economy, as a path to ultimate decarbonization.

With this in mind, an initiative group had set-off to create a proposal for a graduate program first as interdisciplinary engineering PhD degree program within Samueli School of Engineering, with Chemical & Biomolecular Engineering, Materials Science & Engineering and Mechanical & Aerospace Engineering initial participation, with an extension to professional Masters in Engineering (ME) and then as a cross-disciplinary (campus-wide) program to include School of Physical Sciences, with Chemistry, Physics & Astronomy and Earth Systems Sciences participation. The initial thrust is to build on fundamental electrochemistry towards materials and energy applications. Extending the program to include sensors and sensor systems as well as water quality and treatment will naturally lead to inclusion of Electric Engineering & Computer Engineering, Biomedical Engineering and Civil & Environmental Engineering faculty. By this all departments in both schools would become contributive partners in the program. The class schedule for the first accomplish year of teaching is presented in Fig. 1. This flow chart incudes also some planned classes (not realized yet). All though classes are indicted with course number and instructor's name and departmental affiliation. This first 3 teaching quarters have not been formally organized as a program but rather were "self-harmonized" between the faculty as a pedagogical experiment. This presentation will discuss curriculum links and program building challenges.[2]

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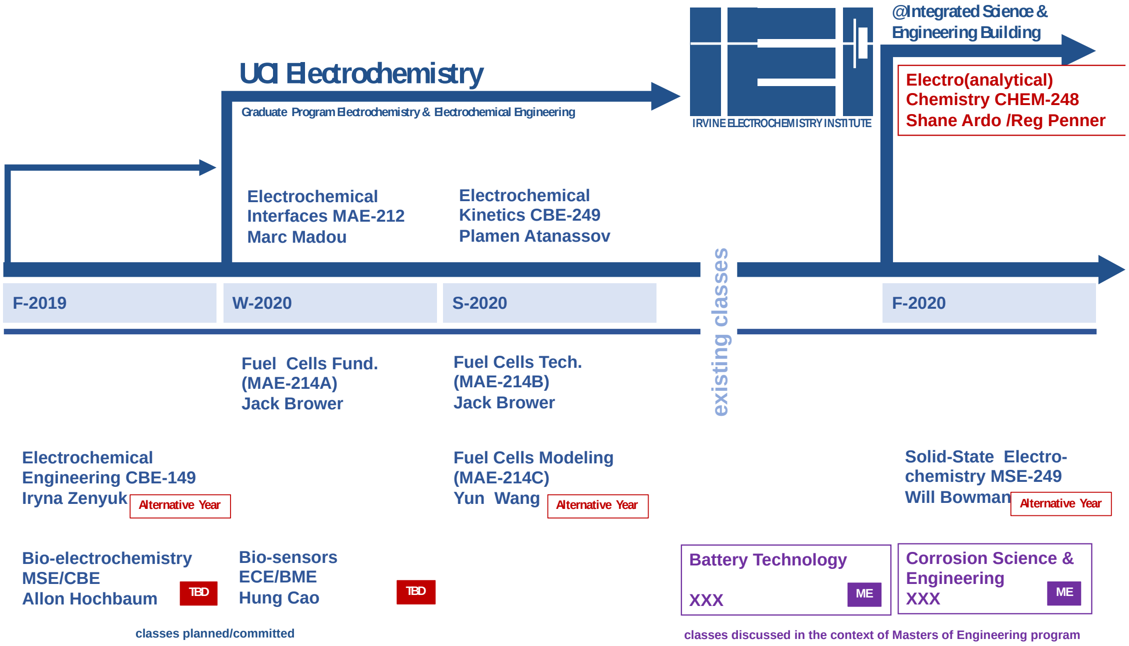
[1] In the United States PhD students must take formal scheduled classes for credit and grade, both core disciplinary classes and technical electives, determining specialization.

[2] The University of California Irvine (as well as most of the UC System campuses) is teaching on a Quarter System: three 10-week long teaching periods: Fall, Winter and Spring.



UCI Electrochemistry

Graduate Program Electrochemistry & Electrochemical Engineering

IRVINE ELECTROCHEMISTRY INSTITUTE

@Integrated Science & Engineering Building

Electro(analytical) Chemistry CHEM-248
Shane Ardo /Reg Penner

Electrochemical Interfaces MAE-212
Marc Madou

Electrochemical Kinetics CBE-249
Plamen Atanassov

existing classes

F-2019

W-2020

S-2020

F-2020

Fuel Cells Fund. (MAE-214A)
Jack Brower

Fuel Cells Tech. (MAE-214B)
Jack Brower

Electrochemical Engineering CBE-149
Iryna Zenyuk
Alternative Year

Fuel Cells Modeling (MAE-214C)
Yun Wang
Alternative Year

Solid-State Electrochemistry MSE-249
Will Bowman
Alternative Year

Bio-electrochemistry MSE/CBE
Allon Hochbaum
TBD

Bio-sensors ECE/BME
Hung Cao
TBD

Battery Technology
XXX
ME

Corrosion Science & Engineering
XXX
ME

classes planned/committed

classes discussed in the context of Masters of Engineering program

Electrochemical Education for a Broad Range of Students in China

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The electrochemical education is encountering great change in the past 30 years in China. The different background of the students and the request from the Ministry of Education to reduce the course hours urgently call for the reform of electrochemical education.

In the 1990's, the electrochemical education in Xiamen University was divided into two parts. One was in the third year physical chemistry, teaching the basis of solution properties, potential and basic electrochemical reaction. The second part was in the four year of undergraduate study, which included kinetics of electrode process, the research methods in electrochemistry, the electrochemical experiments, and applied electrochemistry (including corrosion, electrodeposition, batteries). These courses were also called the specialized courses, which allow the students to have a solid basis of electrochemistry. However, after 2000, the electrochemistry courses in the undergraduate level except that in physical chemistry are removed, which severely discounts the students' understanding of electrochemistry. Furthermore, the students graduated from other universities, who did not have the chance to attend the graduate electrochemistry courses, have very weak electrochemistry background. Therefore, from 2004, the electrochemistry division in Xiamen University started to reform the electrochemistry courses. The specialized courses were integrated into the graduate course, except for the applied electrochemistry as optional courses for both undergraduate and graduate students. The kinetics of electrochemistry was moved to graduate course. The research methods in electrochemistry was integrated with experimental electrochemistry to include the basis of electrochemical interfacial structure, the basis of electrochemical experiments, electrochemical instruments, the transient methods, the steady state methods, the electrochemical impedance spectroscopy, and advanced in situ methods for electrochemistry (including spectroelectrochemistry, infrared, Raman, X-ray and synchrotron based methods, scanning probe microscopies). The students allow to choose at least four experiments from totally 9 experiments, including construction of potentiostat, rotating disk electrodes and fuel cell, cyclic voltammetry and the factors influencing the electrochemical responses, research methods for lithium ion batteries, photoelectrochemsitry, electrochemical in situ methods (infrared, Raman, XRD, SPM). The experiments were arranged in parallel to the theoretical courses. This reform indeed helps improve the electrochemistry basis of the students in Xiamen University.

However, with the increased use of electrochemistry for characterizing the performance of materials for lithium ion batteries, fuel cells, electrocatalysts from materials sciences and inorganic chemistry, we found urgent needs of electrochemsitry from these types of researchers all over China. However, their home universities do not have the resources to teach them the most up-to-date electrochemistry. On considering this situation, we integrated our research methods' course with the materials of the electrochemistry summer school originally run by Southampton group, to run the electrochemical summer school for Chinese students biannually, and recently annually. We invited professors from Xiamen University, Wuhan University, Fudan University, Changchun Institute of Applied Chemistry of CAS, as well as professors from Southampton University to have a tutorial level lectures to selected audiences from all over China, including young faculty members, Postdocs, and PhD and Master students. This greatly help dissemination of electrochemistry for Chinese researchers and this year also to oversea China scientists. We hope in the future such a strategy can be adopted globally.

Living biofilms for sense and respond with electrical current

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Some bacteria establish lines of communication among themselves and electrodes by forming a network of conductive proteins and molecules that carry electrical current, a process known as extracellular electron transfer. Through genetic engineering, such natural electroactive biofilms are being redesigned to create new living microbial electronics for sense and respond applications. We have engineered the biofilm-forming marine bacterium, *Marinobacter atlanticus*, to sense chemicals in seawater and report using electrical current. Biofilm formation and protein expression were first assessed in an electrochemical flow cell in real-time while also measuring current. An isopropyl β-D-1-thiogalactopyranoside (IPTG) inducible system driving yellow fluorescent protein was used to characterize the spatiotemporal activation of protein expression within the biofilm at different stages of growth and induction dynamics. The response time ranged from 30 minutes to 5 hours, depending on the early or late stages of biofilm formation. Fluorescence was detected closer to exposure time and was brighter when biofilms were exposed earlier. More mature biofilms had a slower response time and decreased fluorescence intensity, particularly during transient exposure where most biofilm cells did not express YFP. Chemically induced expression of the *Shewanella* MtrCAB, CctA, and CymA protein electron transfer conduit in *M. atlanticus* resulted in 5 times higher electrical current than the non-engineered strain. A second copy of the native *M. atlanticus* cytochrome *c* maturation system was required for detectable and reproducible expression of these *c*-type cytochromes. To confer bi-directional electronic communication, we are designing inward electron transfer conduits based on the EET pathway of "*Candidatus* Tenderia electrophaga", a marine electroautotroph that grows by carbon fixation using an electrode as an electron donor. Critical EET pathways for "*Ca.* Tenderia electrophaga" were determined by comparison of key proteins across 17 putative members of the family *Tenderiaceae.* Cloning and expression of those identified as membrane-associated, charge-carrying *c*-type cytochromes is currently underway. Combining the *Marinobacter* electrical reporter strain with the inward electron transfer conduit will result in a living electrical material for sense and respond applications.

The Graphite/electrolyte Interface

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Carbon-based electrodes are ubiquitous in electroanalysis and in electrochemical energy conversion/storage, however many of their fundamental properties are quite poorly understood. The heterogeneity of carbon materials is one reason for this. Graphite, particularly the basal plane of pyrolytic graphite, can serve as a useful model material. There has been debate in recent years about the electroactivity of the basal plane relative to the edge plane [1,2]. A related factor, which has also provoked debate in the literature, is the wetting properties of graphite and the susceptibility of contact angle measurements to ambient contamination [3,4].

In this context, the capacitance of graphite electrodes is worthy of re-evaluation. The reference points in this field are the seminal works of Yeager and Gerischer, who studied the capacitance of graphite in aqueous and non-aqueous electrolytes, respectively [5,6]. We have shown recently that capacitance is a sensitive probe of the contamination seen in contact angle measurement [7]. We have also observed specific ion effects within capacitance measurements, which may shed some light on the structure of the graphite/electrolyte interface [8]. As has been noted for single crystal studies of metal electrodes, a key component to understand the metal/electrolyte interface is the structure of interfacial water [9]. Such effects are at least as important at graphite/electrolyte interfaces, where unusual phenomena related to aqueous transport have been reported, including reversible electrowetting effects [10-12].

The future direction of this field will require a “surface science” approach, which has transformed our understanding of the metal/electrolyte interface, to be applied to the graphite/electrolyte interface.

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Strategies for Sustainable Electrochemical Engineering Education: Online Integration

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One of the recent trends in education has to do with Education for Sustainability (EfS). EfS is defined as "a transformative learning process that equips students, teachers, and school systems with the new knowledge and ways of thinking we need to achieve economic prosperity and responsible citizenship while restoring the health of the living systems upon which our lives depend. [1]" Education for Sustainability presents a great opportunity for Electrochemical Engineering, but it raises the question how could programs in Electrochemical Engineering Education (EEE) become sustainable? In addition to this singular challenge, the recent worldwide COVID-19 events have introduced the complexity of limited face to face education to the complete transition to online and in an optimistic aspect, hybrid models. This brings the additional concern to identify how can we effectively transition to incorporate online education in electrochemical engineering while maintaining the classical effectives and interaction with students that face to face education brings into a classroom. Interestingly, effective e-learning can be a platform for EfS [2].

This talk will discuss experiences in developing sustainable electrochemical engineering education programs that involve course curricula, independent design projects, outreach programs [3-4], curricula development for educating science teachers, and the integration of "Online Mode."

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Corrosion of emerging materials

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As technologies rapidly advance, key factors that are critical to materials durability include, (i) materials being utilised in previously unconsidered environments and unique scenarios, and (ii) the durability of emerging materials (and new alloys) is not well understood. The emergence of new materials, and the ability to produce them, has markedly increased in the past decade - owing to a widespread emergence of computational materials design and additive manufacturing. Such aspects will be discussed quite generally, along with specific examples of the durability of emerging materials. A contemporary perspective on what alloy ‘passivity’ may mean in a practical sense is explored; along with new insights into what factors constitute corrosion resistance.

Multi-scale Advanced Characterizations for Solid-State Lithium Batteries

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In the critical area of next-generation batteries, solid-state batteries (SSBs) have drawn increasing attention because of their potential safety, energy-density, and cycle-life benefits.[1] Though promising, they still face challenges that impede their practical application, such as limited ionic conductivity and chemical stability, interfacial stability, electrochemical incompatibility between various components of the SSBs, and thus unsatisfied performance.[2,3] Recognizing this, multi-scale characterization techniques, such as synchrotron and neutron based techniques, are necessary to be employed to study the complex and elusive chemical/physical process in SSBs. Thus, it can offer a deep perspective on various bulk, interface and nanoscale phenomena of the SSBs within the scientific community.

To be specifically, SSBs and the corresponding key cathodes and anodes materials all include complex hierarchical structure and multi-scale interface within the material or devices, those buried structures and interface play critical roles in determining the essential property of the SSBs, such as lithium diffusion, charge transfer, the reactivity and reversibility of the interfacial reaction, structural stability. In this talk, I'm going to introduce the application of synchrotron X-ray spectroscopic, imaging, and neutron scattering techniques, particularly by operando method, on the probing of the fundamental working mechanisms of the key battery materials, components and in SSBs. With gaining a deep understanding of the correlation between the interfacial reaction within the composite electrode materials in multi-scale and the overall electrochemical performance of the SSBs, it inspired us to provide the optimizing strategies for the SSBs.

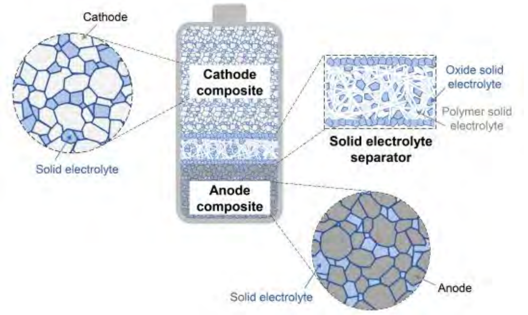

Figure 1. The illustration of the multi-level structure and complex interface between the electrode materials and solid electrolyte within SSBs.

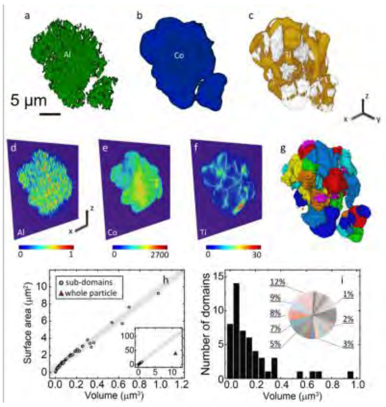

Figure 2. 3D fluorecence X-ray image of $LiCoO_2$ particle with trace Ti-Mg-Al co doping

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A “simple” model system to understand the OER in alkaline media: the Ni-doped $Fe_3O_4(001)$ surface

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Electrochemical water splitting is an environmentally friendly technology to store renewable energy in the form of chemical fuels. Among the Earth-abundant, first-row transition metal-based catalysts, mixed Ni-Fe oxides have shown promising performance for effective and low-cost catalysis of the oxygen evolution reaction (OER) in alkaline media. However, the synergistic roles of Fe and Ni cations in the OER mechanism are unclear[1].

In this talk I will discuss using the well-defined $Fe_3O_4(001)$ surface as a model system for understanding the OER and establishing the structure-reactivity relation on mixed Fe/Ni oxides. Reconstructed $Fe_3O_4(001)$ provides well-defined sites for the adsorption or incorporation of various metal atoms including Ni[2,3]. In an experimental approach going from UHV via neat liquid water all the way to electrolyte and operation conditions, we report how the Ni-modification changes the reactivity. We use surface science techniques in ultra-high-vacuum (LEED, XPS, ISS, STM) as well as in air (AFM), in combination with electrochemical methods (CV and EIS) in alkaline media.

To first test the stability of the Ni-modified $Fe_3O_4(001)$ surface in liquid water, we used a novel experimental setup[4] that allows bringing a UHV-prepared surface in contact with liquid water without exposure to air. Finally, we performed cyclic voltammetry as well as impedance spectroscopy on the Ni-modified surface, and we observed a significant improvement in the OER activity compared to the clean Fe_3O_4 (001). An optimum Fe:Ni ratio in the range 20-40% is found, which is in good agreement with what is observed in powder catalysts[1,5]. This observation makes our model system well suited to study the OER in alkaline media due to its high level of control of the surface and near-surface region, robustness and simplicity.

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Electrochemical Biosensing based on Nanomaterial Labels

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This work reports some examples of electrochemical bioassays based on the use of quantum dots (metal salt nanocrystals) as labels. The principle of the bioassays is that the target biomolecules are selectively labeled with quantum dots of appropriate composition; subsequently, the labels are dissolved releasing the respective metal cations which are quantified by electrochemical stripping analysis [1]. This bioassay format: i) ensures high sensitivity which is due to the synergistic effect of the high loading of each target biomolecule with labelling moieties and the inherent electrochemical signal amplification afforded by stripping analysis ii) enables simultaneous multiplexed detection of more than one biomolecules based on the use of quantum dot labels of different composition.

In this presentation, electrochemical transducers and integrated platforms for nanomaterial-based biosensing are described, fabricated via different microfabrication technologies (such as thin-film micro-engineering approaches, screen-printing, injection-molding and 3D-printing) and representative applications of paper-based, flexible, foldable, fluidic and multiplexed devices are provided [2-7]. Initial results of on-going research in this field will be presented and discussed.

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Solid State Sodium Batteries: from Solid Electrolytes to Functional Device

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Li-ion batteries (LIBs) dominate the electrochemical energy storage technology because of their extraordinary performance, high energy density, and long cycle life. Still, the enormously growing demand of Li due to the expanding market raises concerns about the costs and the availability of lithium in the future, necessitating the development of beyond-lithium electrochemical energy storage concepts. Sodium is among the most investigated alternatives for lithium due to its abundance, widespread availability and much lower costs. The simple replacement of lithium with sodium in liquid electrolyte cells while keeping otherwise similar cell design results however in lower energy densities as compared to LIBs due to a higher molar mass, more positive redox potential and higher reactivity of sodium with liquid electrolytes as compared to lithium. In combination with solid electrolytes, however, much higher energy densities can be expected due to a possible use of metallic sodium as an anode instead of currently used hard carbons, opening new perspectives for the development of Na-based electrochemical energy storage systems [1].

Fundamental prerequisite for the development of high-performance solid state sodium batteries is a sufficiently high total conductivity of all its components at room temperature. The latter includes the ionic conductivity of the electrolyte (simultaneously acting as a separator in solid state batteries), the combined electronic/ionic conductivity of the cathode and the anode half-cells, as well as a high conductivity of key interfaces between the electrolyte and the electrode materials. The total conductivity critically relies on the bulk properties of individual materials, but also on their nanomorphology in the component assemblies as well as on the processing- and operation-dependent interface between the materials [2]. The materials challenge therefore goes far beyond the bulk structure level, including the other fundamental aspects of materials chemistry (such as integration of materials into components, optimization of component microstructure, interface properties), electrochemistry (individual contributions to the total impedance, degradation mechanisms upon cell operation), and engineering (development of processing technology enabling fabrication of optimized components).

We will give an overview of the sodium solid state battery development that spans from the development of solid state sodium conductors to their processing to functional battery components and finally to the fabrication and testing of the complete cells. We will discuss bottlenecks in the battery performance and will show the concepts for the mitigation of critical steps.

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Electrochemical Characterization of Stochasticity in Nanobubble Nucleation

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Gas is evolved in many important electrocatalytic reactions, including those involved in energy conversion and storage, e.g., H_2 and O_2 production from water electrolysis, N_2 and CO_2 generation in fuel cells, and in industrially important reactions, such as the chloralkali process. Gas bubbles formed on electrode surfaces, block the transport of reactants to the electrode surface, creating an additional overpotential and lowering efficiency. Understanding the physical processes that lead to the formation of bubbles on electrode surfaces is therefore of significant interest.

Nucleation is the first-step in the generation of gas bubbles. It requires surmounting the energy barrier represented by the formation of a critical nucleus of 10s to 100s of gas molecules, after which bubble growth is thermodynamically favorable. Overcoming the barrier is a stochastic process, and so characterizing it requires repeated measurements in reproducible conditions.

Driving a gas-evolving reaction at a nanoelectrode generates a controllable supersaturation of gas at the electrode surface, which can induce the formation of a single stable nanobubble.[1] In contrast to work with larger electrodes, in which multiple bubbles can simultaneously nucleate, grow, coalesce, and possibly detach, at a nanoelectrode only one bubble nucleates and can rapidly be detected (temporal resolution <1 ms). As the nanobubble rapidly dissolves on cessation of the current (<50 ms),[2] nanoelectrodes can repeatedly measure the time to nucleate a single bubble; thus characterizing the distribution of times taken to overcome the nucleation barrier.

From these measured distribution of nucleation times, as a function of applied current (supersaturation), we gain physical insight into bubble nucleation, including the shape and number of molecules in the critical bubble nucleus, rates, energetic barrier heights.[3] Measurement of the nucleation of H_2, O_2, N_2, and CO_2 bubbles will be reported.[4,5,6]

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Nanoelectrochemistry for Studying Neurotransmission in Real-Time

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Nanoelectrodes have the advantage of low background charging current, when coupled with scanning electrochemical microscope,[1] it can provide nanometer spatial resolution imaging with high temporal resolution.[2] My group developed the Nano-Interface between Two Immiscible Electrolyte Solutions (ITIES) as a unique analytical platform for the study of ionic species of biological interest such as neurotransmitters on living bio-structures, i.e. single cells and single syanpses.[3, 4, 5, 6, 7, 8] A typical nanoITIES electrode consists of a laser pulled pipet with an orifice in the few nm range that can be filled with an immiscible organic solution for its immersion into biologically-relevant fluids, thus forming a liquid/liquid interface. We studied acetylcholine neurotransmission activity at single neuron structures from the model organism *Aplysia californica*. We employed scanning electrochemical microscopy (SECM) for accurate positioning of our nanoprobes on selected regions of cells and their synapses. By using nanoITIES electrodes, we circumvent challenges in the evaluation of redox inactive neurotransmitters using electrochemical methods.

Our results show that our Nanoelectrochemistry platform, consisting of nanoITIES electrodes and SECM, is powerful for elucidating the mechanisms of cellular signaling.[8] A multitude of information including concentration of transmitters, number of transmitter molecules, dynamics of transmission have been measured in real time.[7, 8] Additionally, we have demonstrated the power of nanoelectrochemistry in determining the number of vesicles per unit area while providing real time transmission information,[8] a big advantage compared to conventional methods using electron microscopy.

Acknowledgement: This research was supported by the National Institutes of Health under Award Number R21NS085665 and National Science Foundation with a CAREER award (CHE 19-45274) to M. Shen.

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Smart scaffolds for electrochemical monitoring of cell cultures

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In bioelectrochemical applications, cells are typically incubated on 2D electrodes. The major limitation of this approach is that planar electrode geometry poorly mimics the natural environment of the cells. 3D polymer scaffolds have been developed to provide a more realistic environment for the cells but these structures usually lack integrated sensor functionality to perform *in situ* measurement in the 3D cell culture. Here, we address these limitations and demonstrate the *in situ* electrochemical analysis of the alkaline phosphatase (ALP) activity in a 3D bone tissue model with integrated electrochemical sensing using 3D pyrolytic carbon microelectrodes. Previously, pyrolytic 3D carbon electrodes have been introduced for electrochemical monitoring of human neural stem cells [1,2].

In this study, a novel approach for fabrication of multi-layered 3D electrodes was developed [3] based on photolithography followed by pyrolysis. 3D culturing of Saos-2 osteosarcoma cells in gelatin hydrogels deposited on 2D and 3D carbon microelectrodes was established (Figure A-B). Saos-2 cells cultured on the electrode express ALP on the surface of their cellular membrane. P-aminophenyl phosphate (PAPP) is added as substrate and hydrolysed by ALP to release p-aminophenol (PAP). The oxidation of PAP to quinoneimide (QI) is carried out during a potential scan in square wave voltammetry (SWV) that generates an oxidation peak current used as signal (Figure C) [4].

In the 3D environment provided by the gelatine hydrogels slower increase of ALP activity was observed compared to 2D cell cultures probably due to reduced proliferation of the Saos-2 cells. Integration of 3D carbon microelectrodes allowed the recording of higher peak currents due to larger surface area of the electrodes (Figure D). For 3D cell culturing for more than one week, a decrease in ALP activity was recorded. This was attributed to the formation of spheroids in the hydrogels, which was confirmed using imaging of the 3D cell cultures with confocal microscopy.

In conclusion, the combination of 3D cell cultures with 3D carbon microelectrodes as smart cell scaffolds is a promising approach for development of *in vitro* cell models.

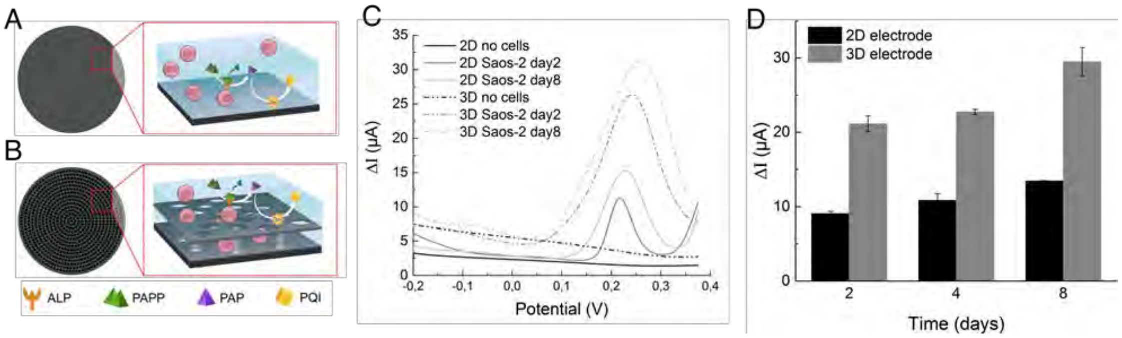

Figure: Schematic illustration of the electrochemical assays: Saos-2 cells are encapsulated in gelatin/TG hydrogel deposited on (A) 2D electrodes and (B) 3D electrodes. (C) Representative SW voltammograms recorded at Day 2 and Day 8 for Saos-2 cells cultured on 2D and 3D electrodes after 1 hr incubation with PAPP. D) Time course of the oxidation peak current due to PAP formation.

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Borohydride Electrooxidation on Nickel: Towards Understanding of the Reaction Mechanism

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Direct Borohydride Fuel Cells (DBFCs) are considered as promising power sources for portable and mobile applications. Their advantages are high theoretical energy density, and high theoretical cell voltage. However, currently available platinum group metal-based (Pt, Pd) electrocatalysts do not allow one to take full advantage of the low standard potential of the BH_4^-/BO_2^- couple (-0.41 V *vs*. RHE) due to the competing faradaic hydrogen evolution reaction and non-faradaic heterogeneous hydrolysis of BH_4^- [1].

We have recently demonstrated that electrodeposited Ni largely outperforms Pt in the borohydride oxidation reaction in the low overpotential interval, both in half-cell and in unit fuel cell configurations [2, 3].

Here we combine electrochemical, *operando* Fourier-Transform infrared spectroscopy (FTIRS), and differential electrochemical mass spectrometry (DEMS) measurements with DFT calculations to propose a tentative mechanism of the borohydride oxidation reaction on Ni.

Acknowledgments
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Hollow Carbon Spheres Codoped with Nitrogen and Iron as Effective Electrocatalysts for Oxygen Reduction Reaction

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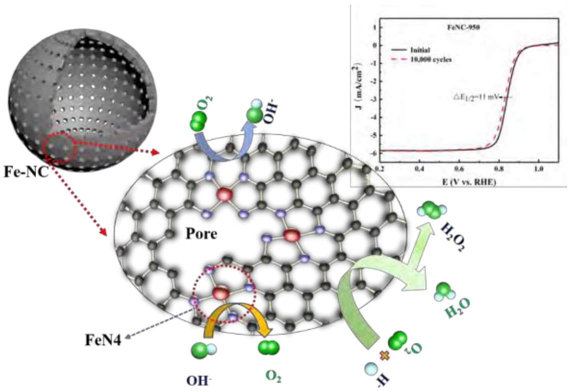
Design and engineering of low-cost, effective catalysts for oxygen reduction reaction (ORR) plays a critical role in the development of fuel cell and metal-air battery. Herein, we report a facile template-assisted strategy for the fabrication of hollow porous carbon spheres codoped with nitrogen and iron species (FeNC) for ORR electrocatalysis. The samples were synthesized via one-step pyrolysis of a core-shell precursor, which was prepared by in-situ growth of a Fe-doped zeolite imidazolate framework (ZIF) shell onto the surface of polystyrene nanoparticles. The obtained FeNC composites exhibited a unique hollow structure with a large surface area, hierarchircal porosity, and abundant FeNx sites. Notably, the sample prepared at 950 ℃ (FeNC-950) exhibited the best ORR activity among the series in alkaline media (with an onset and half-wave potential at +0.94 and +0.84 V vs. RHE, respectively), a performance on par with that of Pt/C and markedly better than those of relevant catalysts reported in recent literature, where ORR proceeded mostly via the efficient four-electron reduction pathway. The FeNC-950 catalyst also displayed superior stability and tolerance to methanol, as compared to commercial Pt/C. The results suggest that high-performance ORR catalysts can be derived by deliberate structural engineering of the metal-organic framework precursors.



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Ce-Containing pH Sensitive Additives for Corrosion Inhibition of Epoxy Coated Steel

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This work discusses the protective role of cerium tri(bis(2-ethylhexyl)phosphate) - Ce(DEHP)3, a pH-sensitive corrosion inhibitor additive in coatings for enhanced corrosion protection. The effect of the inhibitor on the coating barrier properties and corrosion protection performance was studied by electrochemical impedance spectroscopy.

Localized electrochemical techniques was used to probe the self-healing effect at microscopic level. For that purpose, a defect was created in the coating exposing the substrate. The corrosion inhibition effect was studied using localized impedance spectroscopy (LEIS), the scanning vibrating electrode technique (SVET) and localized potentiometry (SIET). Complementary experiments were performed using SEM-EDS.

EIS results carried out for 2 years clearly demonstrated the enhancement of the coating barrier properties in the presence of the additive and its protective role. Localized electrochemical techniques illustrated the self-healing effect and evidenced the corrosion inhibition effectiveness of the pH sensitive additive.

The corrosion inhibition mechanism seems to involve i) a cathodic inhibition effect due to the formation of a protective layer containing Ce-species; ii) inhibition of the anodic reaction due to formation of a stable film of DEHPA and iii) reduction of electrolyte uptake in the coating due to hydrophobization of the coating pores.

Overall, the work demonstrates the improved corrosion protection of epoxy coatings modified with a novel corrosion inhibitor that is activated by local pH changes.

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Environmental-electrosynthetic approach to produce selectively acetic acid from cashew-nut shell liquid waste by using non-active electrode

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Over the past decades, great progress has been made on the electrochemical technologies for the treatment of effluents containing organic pollutants. The electrochemical oxidation (EO) of organics for wastewater treatment, the most popular technology, can be attained in different ways: (i) Direct EO, where electron transfer occurs at the electrode surface without participation of other substances [1]; (ii) Indirect EO where organic pollutants are oxidized through the mediation of some electroactive species generated at the anode surface, which act as intermediaries for electrons shuttling between the electrode and the organic compounds [1]. The efficiency of the process is affected by operating conditions and above all by the nature of the electrode material. In particular anodes with low oxygen evolution overpotential, such as IrO_2, RuO_2 or Pt have "active" behavior and favor the partial and selective oxidation of pollutants (i.e. electrochemical conversion), while anodes with high oxygen evolution overpotential, such as SnO_2, PbO_2 or boron-doped diamond (BDD) have "non-active" behavior and so are ideal electrodes for the complete electrochemical oxidation of organics to CO_2 in wastewater treatment. According to the literature, carboxylic acids are common intermediates in the electrochemical oxidation of several organic substrates or real wastewaters [1]; and these substances are usually neglected. In the past decades, great advances have been made in synthesis of different carboxylic acids [2]. However, expensive or air/water sensitive substrates were usually used in stoichiometric reactions, silanes and/or metallic reducing agents were often required; clean and cheap reductants were necessary to obtain higher yields and multi-steps procedures were also proposed. For this reason, the plan to obtain these chemicals from biomass [3] by electrosynthetic way is of practical importance because the development of green processes to produce compounds with technological application is still a real necessity [4]. In this context, this work aims to combine the distinctive characteristics of a non-active anode to obtain high-added value products (mainly, carboxylic acids) from cashew-nut shell liquid (CNSL) waste, an abundant and renewable raw material in the Northeast Brazilian region. During the environmental-electrosynthetic approach (treatment of effluent to synthetize selectively high added-value products); the concentration of the carboxylic acids was monitored as well as the chemical oxygen demand and energy requirements were determined. The evolution of five carboxylic acids was followed over time for the experiments of the three different current densities using 0.1% of t-CNSL in 1.00 mol L^{-1} NaOH at $Ti/TiO_2RuO_2IrO_2$ anode. At 40 mA cm^{-2}, the most notorious increase in the organic acids concentrations took place during the two last hours achieving selective electrochemical conversion of CNSL for producing acetic acid.

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Transport and Reactivity of Ionic Phases of the Lithium SEI

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The origins of major challenges faced by Li anodes – high reactivity, insufficiently high Coulombic Efficiency, parasitic electrolyte consumption and loss of active Li - can be traced back to the chemical, ionic, and mechanical properties of the native solid electrolyte interphase (SEI). The SEI consists of nominally ionically-conductive, physically-blocking inorganic and organic phases derived from the reaction of Li with the electrolyte such as inorganic LiF, Li_2O, Li_2CO_3, organic semi-carbonates, and polyolefins. After decades of study, the native SEI formed on Li (< 100 nm) remains challenging to experimentally probe, and the individual and collective function of SEI phases is not well-understood. To identify strategies for improvement, understanding of the chemistry, structure, and function of sub-components within the SEI will be beneficial. One challenge has been a lack of empirical data on the properties of individual SEI phases, and specifically when present at a metallic Li interface, where the chemical potential imposed by Li will yield different properties than bulk analogues typically invoked to understand behavior.

In this talk, I present our recent studies of single-component interfaces on Li, which we have conducted to gain deeper insights into the possible roles of common interfacial constituents found in nearly all Li SEI. We have developed synthetic approaches based on gas-phase reactions of Li with oxide- and fluoride-donating reactants that permit introduction of single phases with high spatial uniformity. We show results of controllable growth (10 – 100 nm thickness) of ionic Li_2O and LiF directly onto Li foils. The formed layers are conformal, compact, polycrystalline, and thus serve as model interphases further qualitative and quantitative study. First, electrochemical impedance spectroscopy, combined with interface modeling, is used to extract transport properties (ionic conductivity, diffusivity, charge carrier concentration and activation energy barriers) of $Li|Li_2O$ in symmetric cells with EC/DEC electrolyte. EIS analysis indicated that the ionic conductivity ($\sim10^{-9}$ S/cm) and diffusivity of Li_2O on Li were several orders of magnitude higher than reported values obtained using bulk pellet measurements of Li_2O, which is attributable to the dramatically different chemical, ionic, and microstructural environments. The Li_2O SEI is further studied as a function of synthesis condition, revealing microstructural sensitivities that can be tuned to modulate transport behaviors. Results are compared with single-phase LiF interfaces, and with the native SEI, to isolate chemistry- and structure-specific differences. Finally, I will present our emerging understanding of the chemical stability of these individual phases, Li_2O and LiF, in contact with carbonate electrolytes. Using X-ray absorption near-edge spectroscopy, we have probed the reactivity of ionic SEI phases upon exposure to electrolyte, and find evidence of varying interfacial stability as a function of SEI and electrolyte composition due to reactions at the SEI-electrolyte interface. These results help illuminate the origins of commonly-observed changes in symmetric-cell impedance over hours or days in certain electrolytes, which have lacked chemical specificity to date. The integration of this knowledge to guide design of improved SEI chemistries for transport and stability will be discussed.

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Electrochemical Study and Structural Aspects of New Copper Complexes with Biomimetic Activity

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In this contribution, synthesis and electrochemical characterization of recently synthesized copper complexes (artificial enzymes) mimicking tyrosinase activity are presented. Tyrosinase is a biologically important oxidase, which acts as the rate-limiting enzyme for controlling the production of melanin. It belongs to the group of proteins with a bicopper active center [1]. Unfortunately, tyrosinase has limited lifetime and therefore development of artificial enzymes offers new approach towards the higher stability e.g. in electrochemical sensors [2–4].

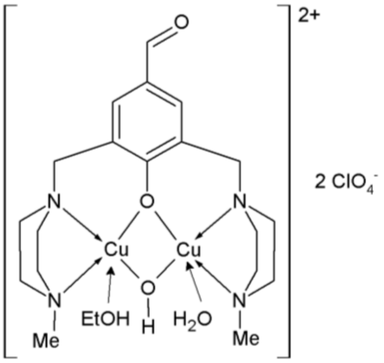

Figure 1: Example of studied $[Cu_2L(OH)(H_2O)(EtOH)](ClO_4)_2$ complex.

Factors controlling biomimetic (catalytic) activity of selected complexes (e.g. on Fig. 1) towards different substrates (3,5-Di-tert-butylcatechol, 2,5-Di-tert-butylhydroquinone, dopamine, serotonin, etc.) are summarized and explained. For this study, electrochemical as well as spectroscopic experiments in aqueous as well as in non-aqueous media were performed. Moreover, another important role plays deposition of artificial enzyme complex on an electrode surface. The obtained results of kinetics of catalytic substrate conversion were compared with those obtained by using enzyme (tyrosinase).

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Fabrication of the Electrochemical Cilostazol Chemosensor with Molecularly Imprinted Polymer Nanoparticles as the Recognition Unit

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In the presented paper, fabrication, and tests of an electrochemical chemosensor for selective determination and quantification of cilostazol is described. Cilostazol, 6-[4-(1-cyclohexyl-1H-tetrazol-5-yl)butoxy]-3,4-dihydro-2(1H)-quinolinone, is an antiplatelet agent and a phosphodiesterase III inhibitor. It is used for the treatment of intermittent claudication (IC), a preliminary symptom of peripheral arterial disease (PAD). PAD is most commonly caused by atherosclerosis. It affects millions of patients worldwide and is associated with significant morbidity and mortality.[1] Fast, simple and reliable method of this drug determination along with its principal active metabolites is important from the point of view of personalized drug dosage. In order to devise selective chemosensor for determination of cilostazol in biological matrices, molecularly imprinted polymer nanoparticles (nanoMIPs) were prepared by precipitation polymerization of the selected acrylate derivatives and were characterized.[2] Furthermore, density functional theory (DFT) calculations were performed for better understanding of interactions between the acylate monomers and the target analyte, and also with its principal metabolites. The result indicated pre-polymerization complex formation mainly through H-bonding.

In the next step the nanoMIPs were immobilized on the gold electrode. Then, the obtained electrodes were characterized electrochemically and spectrally. Moreover, morphology of the obtained electrodes was studied by AFM microscopy. Finally, the analytical tests of the devised chemosensor were performed.

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Highly Energy-efficient Electrochemical Advanced Oxidation Processes Based on Natural Air Diffusion Electrode

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Electrochemical advanced oxidation processes (EAOPs) based on in-situ H_2O_2 electro-generation have acquired an extraordinary significance for the removal of persistent organic pollutants from wastewater [1, 2]. High mineralization efficiency and low energy consumption are the core requirements for the application of EAOPs. The cathode plays an important role in EAOPs, which determines the production of H_2O_2 in the system[3]. However, low oxygen utilization efficiency (<1%) and high energy consumption ((3-20 times electric energy consumption of treatment) are still obstacles to in-situ synthesis of H_2O_2 on the cathode [4].

Herein we propose a superhydrophobic natural air diffusion electrode (NADE) to greatly improve the oxygen diffusion coefficient at the cathode about 5.7 times as compared to the normal gas diffusion electrode (GDE) system and apply it to the treatment of wastewater in EAOPs. NADE allows the oxygen to be naturally diffused to the reaction interface, eliminating the need to pump oxygen/air to overcome the resistance of the gas diffusion layer, resulting in fast H_2O_2 production (101.67 mg h^{-1} cm^{-2}) with a high oxygen utilization efficiency (44.5%–64.9%). Long-term operation stability of NADE and its high current efficiency under high current density indicate great potential for environmental remediation on an industrial scale [5].

In order to promote application of EAOPs for organic pollutants degradation, we studied innovative EAOPs using NADE to improve H_2O_2 production without aeration and enhanced H_2O_2 utilization efficiency in electro-Fenton (EF), photoelectro-Fenton (PEF) and peroxi-coagulation (PC) processes. In the EF process, sulfamethazine (SMT) was removed effectively, but the mineralization degree was not high due to the generation of organic acids which were difficult to be further degraded. While in the PEF process, organic contaminant can be destroyed by the combined action of Fe^{2+}/H_2O_2, UV/H_2O_2 and UV radiation, and more higher mineralization (>83.5%) at low current (50 mA) was attained, which might be attributed to the high H_2O_2 utilization (70-90%), rapid regeneration of Fe^{2+} and photolysis of intermediates. In addition, it was verified that the PEF system had a good adaptability to pH and pollutant concentration. Compared with aeration system, the use of this active gas diffusion cathode in EAOPs significantly reduced energy consumption [6]. 2,4-dichlorophenoxiacetic acid (2,4-D) was efficiently removed by peroxi-coagulation (PC) using NADE as the cathode. In PC using NADE, the 2,4-D removal was 24.6% higher than that of PC using aerated air electrode (AAE), which resulted from higher generation of H_2O_2. Besides, the energy consumption (12.01 kWh kg^{-1} TOC) in PC using NADE was lower than PC using AAE (20.51 kWh kg^{-1} TOC). PC also overcame the narrow pH limitation and showed relatively stable performance upon initial pH of 3-9 when compared with EF system.

The superior performance of NADE and high utilization efficiency of H_2O_2 make it a good application prospect as cathode in EAOPs for environmental remediation.

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Electropolymerization of Catechol and Bio-inspired Analogues – Performance of Thin Films as Biosensing Interfaces

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Robust immobilization of biomolecules is one of the crucial steps when constructing biosensors, since biological activity may be compromised in solid interfaces. Biocompatible polymers, with reactive sites for biocompounds covalent attachment, allow an effective immobilization of the biorecognition element and signal transduction. Polydopamine-based surface modifications have been widely studied [1] and employed in biomedical, energy and industrial applications, including biosensing. However, spontaneous oxidative polymerization does not allow control over structural homogeneity, oxidation state and conductivity of thin films. Recently, electrosynthesis of polydopamine [2,3] has shown to yield better transducing interfaces in enzymatic biosensors than the standard chemical synthesis, highlighting the great potential of electrochemical methods to better tune the chemical and physical properties of polycatechols. Although the catechol group is well known for providing the adhesive characteristics of these films, the role of other chemical functionalities is far less studied and its effects on the final materials properties poorly understood [4].

In this work, we carried out a detailed investigation of the potentiodynamic and potentiostatic polymerization of catechol and distinct bioinspired catecholamines (dopamine, norepinephrine and L-DOPA), disclosing novel insights of their electropolymerization mechanisms. The electrochemical data is supported by electrogravimetry, spectroscopy (FTIR, UV-vis, XPS), atomic force microscopy, ellipsometry and wettability assays. Poly(norepinephrine) displayed the most regular growth and the highest electroactivity. The effect of the different surface chemical groups is accessed towards the electrochemical behaviour of several ionic and molecular species. Furthermore, real-time surface plasmon resonance assays are conducted to assess the adsorption of different proteins to the biomimetic films. Also, the relative ability for polymers *in situ* functionalization is demonstrated with model electroactive compounds and biomolecules (e.g. enzymes, antibodies). Finally, the analytic performance of the different films as amperometric biosensors towards phenolic compounds is also discussed.

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All-solid state ion-selective carbon black-modified printed electrode for sodium detection in sweat

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As reported by World Economic Forum, by 2030, the very nature of disease will be further disrupted by technology. The fourth industrial revolution will ensure that humans live longer and healthier lives, so that the hospitals of the future will become more like NASCAR pit-stops than inescapable black holes. You will go to hospital to be patched up and put back on track, revolutionizing the healthcare from hospital to home-spital. Currently commercially available wearable sensors are aimed at physical sensing to monitor physiological parameters including heart rate, electrical activity of the brain from the scalp and oxygen saturation in arterial blood, but they do not provide any information at molecular levels (chemical sensing). In the research field at academia level, several groups have recently demonstrated that miniaturised devices can potentially monitor electrolytes, metabolites, and heavy metals, directly on the body in various biofluids, such as sweat and wound exudate, however the chemical sensors need to further improved for delivering smart wearable sensors for effective and fast measurement in sweat samples.

In this overall scenario, we developed a miniaturized all-solid state ion-selective electrode for Na^+ detection in sweat sample based on a low-cost fabricated screen-printed electrode modified with Carbon Black to effectively convert the ionic signal through the ion-selective membrane into an electronic signal. Two different membranes were used to modify CB-modified graphite working electrode surface for the selective sodium ion detection and the Ag/AgCl reference electrode for stabilising the potential of reference electrode.

Several parameters were investigated including the volume of carbon black to modify the working electrode, the volume of liquid membrane to modify working and reference electrodes, and the conditioning time. A calibration curve was obtained by potentiometric measurements with a linear response in the range between 10^{-3} M and 1 M described by the following equation $y = 0.068\ x + 0.262$, $R^2= 0.973$. The interference and recovery studies demonstrated the selectivity and accuracy of the sensor developed. Finally, sodium ions were detected in sweat samples collected after physical activity of three volunteers obtaining values equals to (44 ± 4) mM, (55 ± 6) mM, (47 ± 3) mM. in agreement with the physiological range values (e.g. 46.8 mM).

Molecular imprinting of drugs and biomolecules in the conductive polymer matrices – a controlled way of sensor recognition layer fabrication

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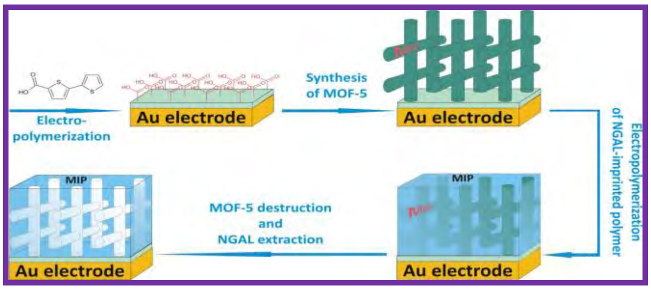
In this contribution application of thiophene and carbazole-based conductive polymers, molecularly imprinted with range of analytes, as the selective recognition layers in chemosensors is described. Combination of electrochemical deposition of molecularly imprinted polymer (MIP) films with selected electrochemical transduction techniques allowed for development of sensors with good selectivity and appreciable limit of detection.



Scheme 1. Formation of NGAL-imprinted porous polymer films with help of sacrificial metal-organic frameworks.

Selective chemosensor fabrication typically requires formation of a recognition layer coupled with suitable transduction element [1]. The recognition layer is not only allowing selective analyte binding but its properties are quite often important in overall sensor performance. Electrochemical deposition of the recognition layer allows for facile control of the process via applied potential, current, as well as solution composition [2]. That way, it is feasible to control deposited film thickness, morphology, porosity or electrical properties, therefore tuning the sensor parameters and response. Furthermore, this method can be easily used to deposit such films on the transduction elements with variety of shapes. Molecular imprinting is an elegant and relatively facile method for devising a sensor selective recognition layer for variety of analytes ranging from small molecules to bacteria and viruses [3]. This approach is based on formation of a pre-polymerization complex between analyte template and functional monomers in solution, followed by its polymerization in presence of cross-linking monomer. Thus, MIP film with molecular cavities with shape, functional groups set-up and properties allowing for selective binding of the imprinted analyte is formed. Application of monomers capable of electrochemical polymerization allows for coupling of this approach with electrochemical deposition of conductive polymers [4]. Such conductive MIPs offer advantages of controlled film deposition, as well as possibility of changing their electrical properties with applied potential, which could allow for development of stimuli-responsive "smart" materials.

Over few years, we have devised and fabricated variety of chemosensors with recognition layers based on conductive polymers molecularly imprinted with variety of analytes. The analytes imprinted in such polymers range from small molecule biomarkers, to drugs, to proteins. In our studies thiophene and carbazole derivatives were used as functional and cross-linking monomers. Deposited conductive MIP films morphology and properties were studied and analytical parameters of the final chemosensors were tested. Possibility of controlled formation of highly porous polymeric structures is also presented. Finally, advantages and disadvantages of this approach are discussed.

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Sewage Sludge Treatment by a Novel Electrochemical Technique

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Sewage sludge is the main waste generated in the wastewater treatment. Solid waste mismanagement is posing the risk of environmental pollutions due to releasing the harmful pathogens (e.g Escherichia coli, etc.). Anaerobic digestion is the typical technology for sewage sludge treatment. However, sludge hydrolysis is the limiting step for sludge degradation in the anaerobic digesters. Therefore, it results in long residence time in the digester reactors (approximately 20-30 days) and considerable energy consumption. Moreover, it has been reported that waste disposal is a cost and energy intensive process and accounts for approximately 50- 60 % of the operational cost in the wastewater treatment facilities. Hence, new treatment methods need to be developed to decrease energy consumption and capital cost.

It has been shown that alkaline treatment is efficient for the sludge biodegradation. Besides, electrochemical oxidation of the biomass is the clean alternative technology for sludge disintegration and pathogen destruction. To overcome the conventional treatment method limitations, our research group has developed a novel, energy-efficient pathway for wastewater treatment by integrating alkaline and electrochemical oxidation techniques at room temperature. The results showed a considerable solid reduction and energy consumption when compared to similar research studies. The biosolid characterization after treatment represented the potential of generating value-added chemicals in the liquid phase and the successful removal of pathogens for safe disposal or agriculture application.

Innovative Structuration of Carbon-Ink Electrodes for Electrochemical Detection

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Electrochemical sensors are powerful and versatile analytical tools in different fields, for example medical analysis and healthcare application. Today's requirements on them correlate with the advances in electrode design: The fabrication of miniaturized electrodes allows for the design of small-scale sensors or arrays, respectively, corresponding to the demand of portable and even implantable "point-of-care" devices for monitoring application, as well as the analysis of small sample volumes [1].

Electrode miniaturization, however, imposes a physical limitation linked to the reduction of the electrochemically active electrode area. For amperometric sensors (biosensors), this implies a loss in faradaic current, resulting in a lower signal. In case of solid-state Ion-Selective-Electrodes (ISE), the charge storage capacity and the quality of the charge exchange on the selective membrane/collector interface are reduced, leading to a degradation of sensitivity, stability, dynamic range and limit of detection. While the impact of electrode structure has been profoundly studied [2] and numerous interesting approaches exist on the laboratory scale, the majority involves complex, multi-step processes of time-consuming nature, which thus seem unsuited for the production on a larger scale. Printing techniques on the other hand, which are well established in the industrial production of low-cost solid-state sensors, are not designed to generate structured electrochemical interfaces.

In this work, commercial carbon ink, suited for screen-printing, was deposited on polymer substrates and subjected to a process-oriented, environmentally friendly treatment (patent pending) with the aim to structure the surface and increase the electrochemically active area. Scanning Electron Microscopy studies (SEM) confirm the surface structuration (Fig. 1a), as well as the generation of a porous network in the bulk. Electrochemical characterization consisted of Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). Results were compared to a cured, unstructured electrode, for which fast, reversible electron transfer and semi-infinite linear diffusion were observed. Upon treatment, the reversible nature of the charge transfer was conserved (Fig. 1b); however the voltammetric response indicates a temporal characteristic and a combination of semi-infinite and thin-layer finite diffusion [3]. Faradaic and capacitive currents increased by more than one order of magnitude. Impedance studies confirmed the pronounced capacitive nature of treated electrodes (Fig. c). ISE and amperometric sensors containing as-structured electrodes are currently under study and the potentiometric measurements already presented promising results.

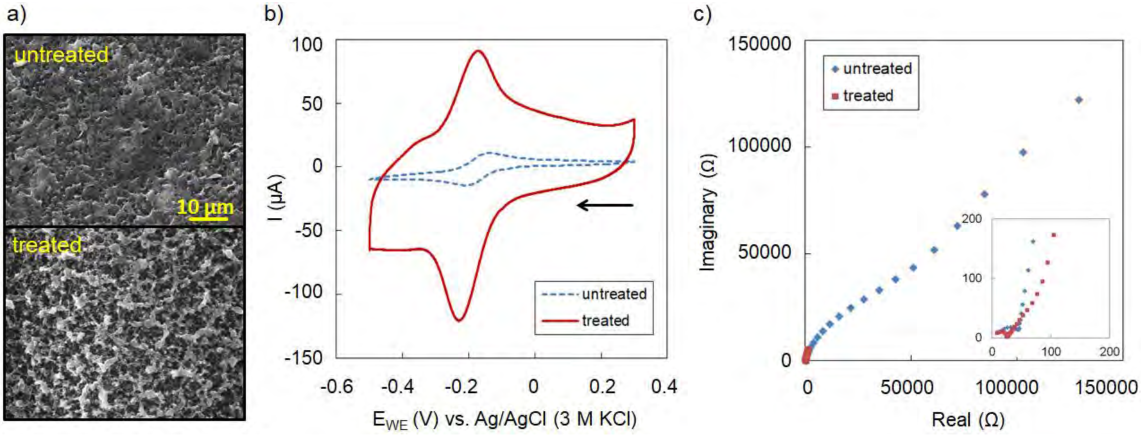

Fig. 1: Untreated and treated electrode deposit characterization, a) SEM: V_{acc}=30 kV, V_{extr}=5.6 kV, b) CV: 1 M KCl, 1 mM $Ru(NH_3)_6^{3+/2+}$, 50 mV/s, c) EIS: 1 M KCl, 0.1 Hz to 1 MHz.

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Structure-Dependency on the Photoelectrochemical Performance of Two-dimensional Transition Metal Dichalcogenides

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The two-dimensional (2D) semiconductors, the transition metal dichalcogenides (TMDCs), have received great interest during the last decade because of their high chemical stability and good electrocatalytic properties [1]. The photoelectrochemical (PEC) properties of 2D nanoflakes depends on the structural properties (the number of layers, the basal-planes or edges) [2-4]. We need to understand their fundamental PEC properties in the function of their structural properties, using a microscopy-based approach with spatial resolution.

Firstly, I will show our recently developed custom-designed PEC-microscope setup. The deposited 10–50 μm sized microdroplet acts as an electrochemical cell on the chosen sample area of the 2D flake, which will be illuminated by a spot at 25–50 μm in diameter. The TMDC nanosheets (MoS_2, $MoSe_2$, WSe_2) were mechanically exfoliated to get bulk, few-layered, and monolayer specimens. Additionally, liquid phase exfoliation was used to prepare bulk and few-layer TMDC dispersions. The number of layers, and defect types in the separated nanosheets were characterised by Raman spectroscopy and atomic force microscopy. I present the use of model reversible redox species to mimic photoelectrocatalytic processes, proving the differences between basal-planes and edge sites. Then, I show the effects of varying the number of layers and role of the edge-sites on the light harvesting, charge transport, and recombination properties with photoelectrochemical measurements unfolding reasons behind the poor PEC activity of exfoliated 2D samples.

Finally, I demonstrate the effect of structural domains for PEC performance of 2D materials in three points. i) The photocurrent losses with growing the fraction of the heterogeneous surface (edge sites), with the parallel rise of dark currents. ii) The higher defect density changes the PEC activity for water oxidation as well, the activity is found to be larger for both basal-plane of bulk and few-layer $MoSe_2$ in the presence of hole scavenger, so the higher photocurrent cannot be harvested for oxidation. iii) The LPE produced $MoSe_2$ and WSe_2 bulk and few-layer flakes in kinetic control free water reduction and oxidation, achieving only μA cm^{-2} current densities. This decrease in the PEC performance can be explained by the growing of defect densities, because of the number of edge sites is increased and the lateral size (area) is decreased of LPE flakes.

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Designing Cells to Detect Redox Potential Gradients within Conductive Biofilms and Rectify Electron Flow

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Geobacter sulfurreducens can grow as a conductive biofilm when utilizing a poised electrode as an electron acceptor. These biofilms show redox hydrogel-like behavior in scan rate analysis, confocal Raman spectroscopy, and interdigitated array electrode redox-gating experiments. Recent NanoSIMS imaging revealed a gradient of anabolic activity within these biofilms, with the highest activity closest to the electrode[1]. Based on the diffusional limitations of electron transport within redox hydrogels and this evidence of a metabolic gradient, we hypothesized that a redox potential gradient exists within these biofilms, becoming lower with distance from the electrode until it restricts respiration. We previously reported that there are two routes out of the inner membrane quinone pool in *G. sulfurreducens*, one that predominantly functions above redox potentials of 0 V vs. SHE[2], and another that only operates between redox potentials of 0 and -0.2[3]. With the discovery of a third pathway that only is expressed at redox potentials below -0.2 V vs. SHE, we can construct double and triple mutants which will only grow in specific redox potential windows. We also screened a series of GFP-based reporters driven by constitutive or redox-dependent promoters, to produce mutants expressing green, red, or cyan fluorescent proteins at levels detectable by standard fluorescent or confocal microscopy after ~1 min of oxygen exposure. When two strains of *G. sulfurreducens* able to grow at different redox potentials are mixed together, cells favoring high redox potential only colonize the electrode surface, while cells favoring lower redox potential are only found at the top of the biofilm, away from the electrode surface. Similar results are obtained when a low redox-potential dependent promoter is used to drive GFP expression: expression is only detected far from the electrode. These results support a model of differential metabolic states within biofilms, with cells closest to the electrode being most metabolically active due to high redox potential. By cultivating these mutants on arrays of interdigitated electrodes, alternating bands of cells only able to respire at low- or high-potential can self-assemble within 48 hours, and produce living conductive materials that rectify electron flow to only one of two drain electrodes.

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Chromium and Tungsten Benzocondensed Heterocyclic Aminocarbenes: Comparison of Redox Properties and Reactivity

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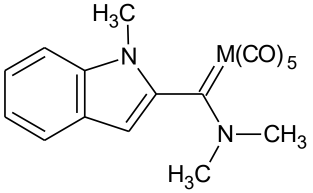
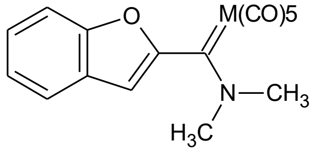
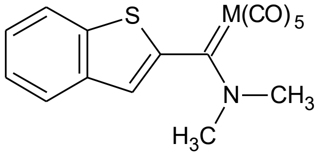
Carbene complexes are characterized by presence of a formally double bond M=CR$_2$. In electrophilic carbenes of Fischer type, the M$^{\delta-}$ = C$^{\delta+}$ polarity of this bond is typical. An extended study of mononuclear complexes (CO)$_n$M = C(NR')R showed that there are two rather independent redox-active centers present: oxidation is aimed at and influenced by, the metal atom, while reduction proceeds on the carbene moiety. Analogous behaviour was found at compounds bearing condensed benzene-heterocycle substituent.

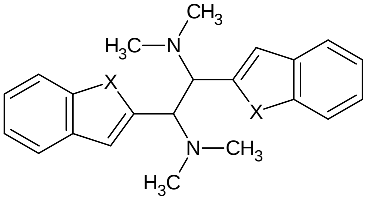
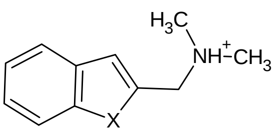
Studied compounds, M = Cr, W		
		
Cr-bpyr; W-bpyr	Cr-bfur; W-bfur	Cr-bthi, W-bthi

The molecules were studied using cyclic voltammetry on GC, Pt, and HMDE electrode, by IR and UV-Vis spectro-electrochemistry. Preparative electrolysis was performed using Hg pool working electrode, the products were identified by MS and IR spectra.

The oxidation process is quasi-reversible, it proceeds in two steps and oxidation potentials of the compounds with the same central atom lay within 50 mV range, depending on the substituent; it increases in sequence M-bfur < M-bpyr < M-bthi. For W compounds, oxidation potentials are by 250 mV more positive. The inductive influence of the heterocycle itself (heteroatom) is evident.

The reduction of the presented compounds is impacted by substituents of the carbene carbon. It proceeds at similar potential values for both Cr and W compounds, potential range is about 200 mV. The most negative E_{red} value belongs to M-bpyr, the reduction of M-bfur and M-bthi proceeds at very similar potential values.

The most pronounced difference between chromium and tungsten compounds was observed in their reductive electrolysis products. While chromium complexes reduction leads to a dimeric product, the electrolysis product of tungsten complexes consists only of monomeric products. Similar behaviour has been described [1] for chromium complexes substituted by simple heterocycles.

Reductive electrolysis product of Cr complexes	Reductive electrolysis product of W complexes
	 X = N(CH$_3$), O, S

Acknowledgement: Financial support from specific university research (MSMT No 20-SVV/2019) is gratefully acknowledged.

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Chemomechanical Models for Locally Non-neutral Solid Electrolytes

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Recently our group has focused on developing, parameterizing, and accurately solving models that describe chemomechanical phenomena in electrolytes, *i.e.*, situations in which stress in a material may be coupled with its electrochemical state. Our approach, based in irreversible thermodynamics [1], has followed the general transport modelling programme initiated by Newman [2], but extends that theory to account for a phase's compressibility or elasticity, as well as local deviations from electroneutrality.

Although we have produced informative preliminary results by applying the chemomechanical theory in idealized cases [3,4], a number of foundational problems remain unresolved. The development of thermodynamically consistent flux laws applicable to non-ideal, non-neutral, elastic electrolytes poses several problems at the most elementary level. One desires a straightforward parameterization of electrochemical potentials in terms of familiar thermodynamic properties, such as partial molar volumes and Darken factors for dissolved salts and solvents, and a transport model that includes familiar transport properties, such as Fickian salt diffusivity, ionic conductivity, and cation transference number. When electroneutrality is relaxed, the standard definitions for the transport properties becomes substantially more complicated [5], and the thermodynamic property set becomes ambiguous [6]. Further, it is unclear how classical properties involved in electrostatic equilibria, such as permittivity, or elastic properties, such as the bulk modulus, should be brought into models in a self-consistent way.

This talk will address the general problem of multicomponent mass-transport modelling for non-isobaric, non-neutral elastic electrolytes. We will discuss a new constitutive framework that can be deployed to formulate the electrochemical potentials, which brings colligative properties measured in an electroneutral state naturally into the non-neutral transport model. These new 'core chemical potentials' relate to the Guggenheim electrochemical potentials through a straightforward sequence of linear transformations, which can be expressed in terms of matrix multiplications and depend only on the species charges. The core potentials can be mapped into the popular electrochemical-potential frameworks developed by Guggenheim [6], Smyrl and Newman [2], and Kokotov [7]. The new theory allows thermodynamically consistent modelling of, for example, voltage-dependent interfacial capacitance in concentrated double layers, transient diffusion driven by the Gibbs–Donnan effect, or stress diffusion in solid ion conductors.

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Constant Potential Amperometry for Detection of Electroinactive Ions and Molecules with Conducting Polymer-Based Electrodes

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It is well known that conducting polymers can serve as solid-contacts of ion-selective electrodes. To improve the performance of solid-contact ion-selective electrodes (SC-ISEs) alternative to classical potentiometry readout principles have been proposed [1].

The constant potential techniques seem to be the most promising and solving the main problem of background drift and potential instability of potentiometric SC-ISEs. However the constant potential amperometric flow-injection analysis (FIA) for conducting (electroactive) polymer-based sensors has not been reported yet. The proposed earlier amperometric FIA uses potential step methods. Thus the sensor readout principal is voltammetric rather than amperometric.

We report on the flow-injection amperometry at constant potential with polymer-based sensors for detection of electroinactive inorganic ions and organic molecules. Polyaniline, poly(3,4-ethylenedioxythiophene), Prussian Blue films and nanoparticles were used as solid contacts of K^+ and Na^+-selective electrodes. Sensors based on self-doped polyaniline, substituted with boronic acid, without ion-selective membranes were applied for amperometric detection of electroinactive organic compounds (lactate, fructose), due to selective interaction of diol- moieties with boronic acid group.

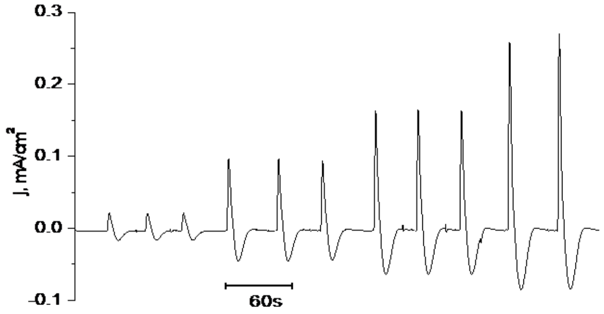

Fig.1. Amperometric response of PEDOT-modified sensor towards injections of KCl (1, 5, 10, 15 mM).

Regardless of the polymer support the amperometric response of the electrode towards analyte injection is a couple of oppositely directed peaks (Fig.1). The peak current is dependent on the concentration of analyte. We've shown that in a constant analyte solution flow mode only one current peak is observed. Thus the emerging current is a result of polymer oxidation/reduction reaction in order to maintain the constant electrode potential. Notably that current direction (cathodic or anodic) depends on the ability of ion to interact with the polymer functional groups. The influence of applied potential also has been investigated. Two cases were considered: 1) polarization of the electrode / polymer interface due to ion transfer through the polymer / solution interface; 2) specific interaction of ions or molecules with polymer at the polymer / solution interface. The suggested technique was applied for flow-injection analysis of human sweat. The successful amperometric detection of lactate with boronate-substituted polyaniline-based sensor has been performed.

The constant potential amperometry provides the advantageous analytical characteristics: the signal-to-noise ratio in amperometric mode is 20–25 times higher in comparison to potentiometric one [2]. Thus it is a promising method for detection of ions and molecules with polymer-based sensors and SC-ISEs.

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Tuning surface composition and transformation pathways in atomically-flat $LaNiO_3$ thin films for enhanced water electrolysis

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The need for highly efficient catalysts for sustainable energy has led to remarkable improvements and insights in the design rules for (electro-)catalyst materials. Many successful examples employ perovskite-type oxides (ABO_3) because of the large tunability of chemical and electrical properties. Because of inherent differences in surface and bulk properties, further advances in catalyst stability and activity engineering necessitate the derivation of surface-composition-activity relationships in addition to descriptors based on the bulk properties.

Single crystalline surfaces offer the ideal platform to derive such relationships. They enable direct comparison to surfaces investigated in density functional theory (DFT), which are typically limited to a single facet that may or may not be present in catalysts fabricated using traditional routes. Epitaxial thin films allow investigation of perovskite catalysts fabricated with unit-cell precision.[1–3]

Here, we will demonstrate surface-composition-activity relationships in epitaxial $LaNiO_3$ thin films, which are atomically flat both before and after application as electrocatalysts for the oxygen evolution reaction (OER) during water electrolysis, and which possess a controllable surface cationic composition. For the $LaNiO_3$ surface, the Ni-termination is electrocatalytically active and undergoes a surface transformation that preserves the surface cation stoichiometry of the as-prepared state, while La-termination leads to high overpotentials and eventual failure. Our work thus suggests that the (meta)stable surface layers evolving at the solid/liquid interface, and therefore the electrocatalytic activity, can be selectively adjusted through the choice of as-synthesized surface composition.

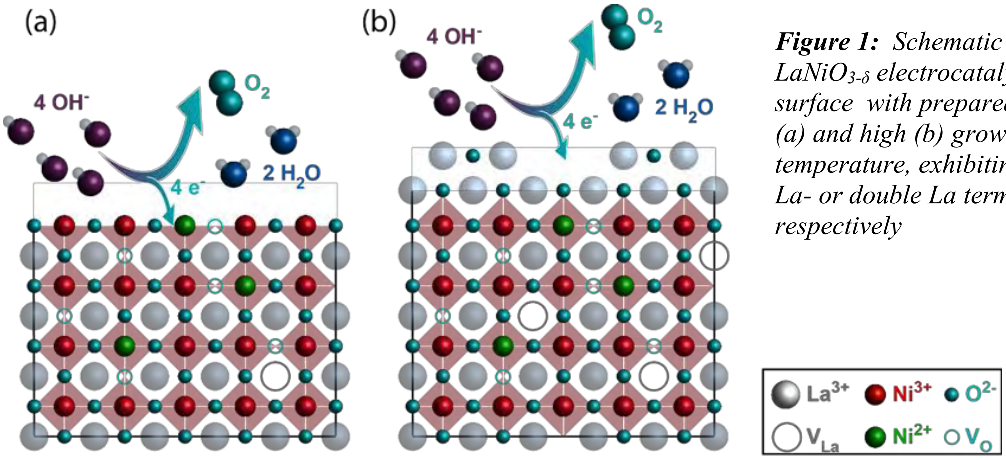

Figure 1: *Schematic of a $LaNiO_{3-\delta}$ electrocatalyst surface with prepared at low (a) and high (b) growth temperature, exhibiting Ni- and La- or double La termination, respectively*

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Teaching Impedance using a Python-Based Regression Program

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Interpretation of impedance spectra requires in principle an evaluation of the error structure and a process model that accounts for the proposed reactions and physics. The measurement model was developed in our group in the 19990s as a tool to extract the stochastic part of the impedance measurement from repeated measurements and to assess the consistency of the measured impedance with the Kramers-Kronig relations.[1-3] Our measurement model approach has been difficult to explain, in no small part because our original measurement model program, written in a combination of FORTAN and Matlab® programming languages, was not generally available. We were reluctant to share the code because each new version of Matlab® broke the Matlab® part of the program, and a part of the FORTRAN code was not ours to share.

A new version of the measurement model has been written in the Python language and will be made available under the open-source license GNU GPL Version 3, which allows free use for scientific purposes but limits commercial use. The new code was written from the ground up in Python, although some portions of the backend libraries, such as numpy, use C. Unlike many Python-based impedance regression programs, the measurement model program provides a graphical-user-interface that facilitates navigation through the different stages of the measurement model analysis. This program also allows regression of arbitrary functions to impedance data. Rather than employ electrical circuit components such as resistors and capacitors, this part of the program is equation-based. The formula is input as Python code and may make use of imported Python packages. The equation-based approach enables regression of a broad range of models.

We have found that, by using this Python-based measurement model program, students develop a better appreciation for the power of impedance spectroscopy and for the importance of error structure in impedance measurements. The objective of this presentation is to demonstrate the program and suggest ways in which it can be employed in teaching impedance spectroscopy. Our goal is that, by providing the tools needed for a more sophisticated analysis of impedance data, we will allow students to take full advantage of the information that can be extracted from electrochemical impedance spectroscopy measurements.

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Spatially-Controlled Photoinduced Redox Processes at Organic Semiconductor/Liquid Interface Revealed by Scanning ElectroChemical Microscopy

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Reactive oxygen species (ROS) are produced in living cells in several physiological and pathological processes [1,2]. Reactive oxygen species production by organic polymer upon photostimulation is gaining more and more interest for its high throughput capability, selectivity and resolution. Organic copolymers are generally good photo-transducers, with tunable optical properties, good photocatalytic efficiency and characterized by excellent biocompatibility. Nanoparticles of poly-3-hexyl-thiophene (P3HT) have been showed to be internalized within the cell cytosol and generate ROS upon photo-stimulation [3].
We employed electrochemical approaches, such as Scanning ElectroChemical Microscopy (SECM), to measure ROS production by P3HT thin films and explored the impact on H_2O_2 production in the presence of a model cellular redox protein, Cytochrome C [4]. Spatially-controlled illumination of substrates and simultaneous detection of hydrogen peroxide production at the micrometric scale were achieved by coupling SECM with a fluorescence inverted microscope. Hydrogen peroxide was measured with high sensitivity employing platinized-microelectrodes. ROS were recorded in dark and upon illumination in close proximity of the P3HT thin film substrate and compared to bare ITO substrates. We resolved the profile of H_2O_2 production by P3HT thin films upon photostimulation at the micrometric scale.
The interaction between P3HT thin films and Cytochrome C (in the dark or upon photostimulation) was investigated exploiting our SECM/fluorescence microscope apparatus: our results indicate that upon photostimulation Cytochrome C is reduced at the organic semiconductor/liquid interface.

Acknowledgements
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Determination of ten underivatized biogenic amines by ion pair chromatography using potentiometric detection

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Biogenic amines are organic bases of low molecular weight with a high impact in food quality control. The most common analytical methods used for their assessment are based on liquid chromatography coupled with spectrophotometric detection, such as UV-vis and fluorometry [1]. However, the high polarity of biogenic amines difficult their retention on conventional reversed-phase chromatographic columns while their low detectability by spectrophotometric techniques hinders the detection limits and sensitivity, which requires additional derivatization steps to circumvent these drawbacks.

Alternatively, electroanalytical detection offers high sensitivity with simple and inexpensive instrumentation, without the need for derivatization steps. Amperometric and conductimetric detectors have been proposed for the determination of biogenic amines after separation by HPLC but those based on potentiometry seem overlooked [2].

In this work, a novel RP-HPLC method for the determination of ten underivatized biogenic amines is proposed based on ion-pair chromatography combined with a miniaturized potentiometric electrode inserted in a low-dead volume wall-jet flow-cell. Aliphatic amines – methylamine, ethylamine, cadaverine, putrescine, spermidine, and spermine as well as the aromatic heterocyclic amines - histamine, tyramine, phenethylamine, and tryptamine were selected. It was used an amine-selective electrode based on cucurbit[6]uril as an ionophore, enhanced with MWCNT's for a better improvement of the ion-to electron transduction. A gradient elution method with butane 1-sulfonic acid as ion-pair agent, and acetonitrile as an organic modifier, flows through a Luna® Omega 5µm Polar C18 150x4.6mm column with a flow-rate of 1.2 mL min^{-1}. The optimized method allowed the separation of all studied amines with a good resolution. The total analysis time was 25 min.

The proposed method was validated according to the requirements of ICH (International Conference on Harmonisation). The analytical signal was transformed by using the equation $tR = 10^{E/S} - 1$, where E is the potential (mV) and S the slope of the typical Nikolsky-Eisenman equation [3]. When tR was plotted against the analyte concentration a linear regression model was obtained with R^2 varying from 0.983 to 0.996. Repeatability was evaluated at three different concentration levels of standard solutions. The relative standard deviation (RSD) values were lower than 10.9%. Detection limits ranged from 9.3 to 60.7 µg L^{-1} and quantification limits from 31.1 to 202.3 µg L^{-1}.

Biogenic amines in the different food samples are yet to be determined.

Acknowledgments

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Surface Modified Carbon Nanomats Provide Cationic and Anionic Rectifier Membranes in Aqueous Electrolyte Media: A Prospect For Desalination

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The current water crisis, caused by climate change (and lack of rainfall), has prompted researchers to find alternative and efficient ways for converting sea water into fresh drinkable water. Ionic diodes have been found recently to offer one such approach [1,2]. In the current work, carbon nanofibers (CNFs) are converted from cationic current rectifiers to anionic current rectifiers by surface modification with boron and amine functional groups using hydrothermal means (forming BNCNFs, with boric acid, generation-3 poly(propylene imine) dendrimer, and urea. To confirm surface charge, morphological changes and carbon nanomat thickness, zeta potential analysis, transmission electron microscopy (TEM) and scanning electron microscopy (SEM), were used. When a dispersion of surface modified carbon nanofibers in DMF is drop-cast asymmetrically to form nanomats onto laser drilled microholes (5, 10, or 20 µm diameter) of poly (ethylene terephthalate) substrates and immersed into aqueous electrolyte solutions, anionic diode behaviour is observed (in contrast to pristine carbon nanofibers, which exhibit cationic diode behaviour). The effects of electrolyte type, ionic strength, and microhole diameter on ionic diode performance were investigated using cyclic voltammetry, chronoamperometry, and impedance spectroscopy. Future applications in desalination are proposed.

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Electrochemical Protocols for determining Gallic Acid and Caffeic Acid in Winery Cellar Effluent

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Phenolic compounds have been enlisted by the United States Environmental Protection Agency (USEPA) and the European Union (EU) as pollutants of priority concern. This enlistment is due to the fact that these chemicals are noted to be toxic and have severe short- and long-term effects on humans and animals. The occurrence of phenolic compounds in the aquatic environment is therefore not only objectionable and undesirable but also poses a danger as far as human health and wildlife are concerned.
South Africa is known to have used and abused most chemicals listed by developed and developing countries as endocrine-disrupting chemicals. Endocrine disrupting chemicals have been reported in water. The winemaking industry produces large volumes inorganic wastewater that pose an environmental threat if not treated correctly. The increasing numbers of wineries and the demand for wine around the world are adding to the growing problem. This increase has further aggravated the pressure which the industry exerts on natural resources such as water, soil and vegetation. [1].
No two effluent produced by Wine estates are the same. This variation is as a result to the differences that exists processing techniques, regions of farming and cultivar of grapes used. Thus electrochemistry is seen as a clean, versatile and powerful tool for the detection of pollutants in water and making these sensors a good tool for testing pollutants in winery water waste.
Wastewater is regarded as the most significant environmental risk at wineries and because water is a limited natural resource in South Africa, water monitoring and saving should be encouraged [2].

The aim of this study was to design, construct and develop a tyrosinase biosensor modified on a Boron-doped Diamond (BDD) platform in order to determine the levels of polyphenols in real aqueous winery wastewater samples. Specifically Gallic Acid and Caffeic Acid was chosen as the polyphenols of study. The BDD surface was electrochemically coated with polythiophene (Pth) film, containing in-situ deposited tyrosinase (Tyr). Electropolymerization of Pth was done via cyclic voltammetry (CV) at 50mV.s^{-1} versus Ag/AgCl). The morphologies of the composite films where studied by scanning electron microscopy (SEM). Detection of polyphenol substances was done and square wave (SQW). Further Uv-Vis was used to verify the conservation of polyphenols during these electrochemical; and enzyme oxidation steps.

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Capacitive Desalination with Sulfonated Nanoporous Carbon Electrodes

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Capacitive deionization (CDI) is an emerging technology for the removal of charged ionic species from water and is often applied to brackish water desalination and water softening [1]. CDI typically uses inexpensive nanoporous carbon electrodes to desalinate, and carbon surface functionalization can increase the adsorption capacity, rate, and selectivity [2]. Sulfonation, the attaching of strongly acidic sulfonic groups to the carbon material, creates a surface that is strongly negatively charged in an aqueous environment at all electrolyte pH values. This property is highly desirable for CDI, yet such electrodes are largely unexplored.

In our study, the sulfonated activated carbon fibers (SACFs) are prepared using the following protocol. Two grams of activated carbon fibers (ACFs) are sulfonated with 100 ml of 20% fuming sulfuric acid for 24 hours. The product is then washed with hexane and ice water, and dry in the oven at 50°C. The final product is referred to as SACFs. Fourier-transform infrared spectroscopy (FTIR) tests were performed for both ACF and SACF samples. An acid-base titration was used to quantify the nanopore chemical charge concentration of the sulfonated material. The result are shown as in Figure 1 (a), which are obtained from the fitting titration data to a micropore EDL model described in [3]. Results show sulfonation imparted a significant strong acid group micropore concentration, $c_{A1,0}$, of 2.75 M.

CDI tests were conducted in a flow-through electrode CDI cell with either two ACF electrodes or one ACFs anode and one SACFs cathode. We used a 20 mM NaCl feed solution, 4 hours for each charge-discharge cycle, a charge voltage of 1 V, and discharge voltage of 0 V. In Figure 1 (b), we show measured salt absorption, demonstrating that the SACFs show enhanced performance in CDI specific salt capacity comparing to pristine ACFs.

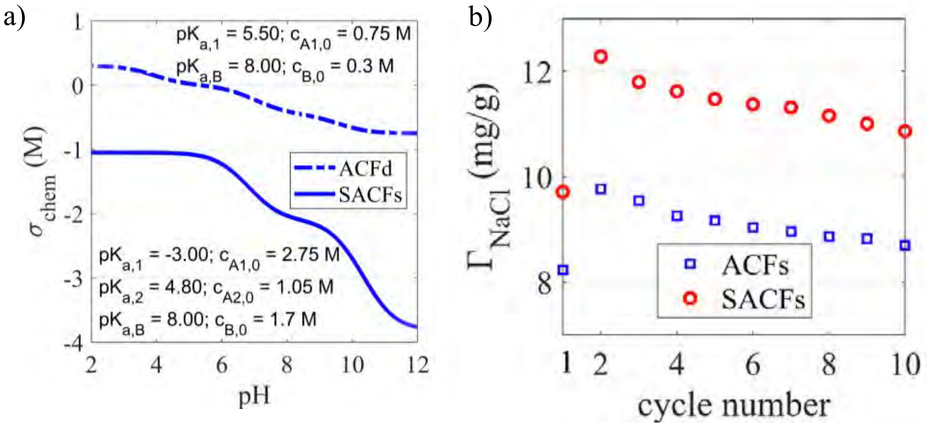

Figure 1: a) Nanopore chemical charge concentration versus pH, obtained from titration model to data fitting, pK_a and $pK_{a,B}$ are equilibrium constants for acid and a weak basic groups, c is the concentration of each group in the unit M, i.e., mole per micropore volume. b) Measured salt electrosorption in a CDI cell versus cycle number, using either two ACF or one ACF and one SACF electrodes.

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Enhancement of Electrooxidation of Simple Organic Fuels at Noble Metal Nanoparticles Supported onto Mixed-Metal-Oxides

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There has been growing interest in utilizing small (simple) organic molecules, as alternative fuels to hydrogen, in electrochemical energy conversion systems. In addition to ethanol (biofuel), that can be ideally oxidized to carbon dioxide thus delivering twelve electrons, recent important systems include dimethyl ether as well. But realistically the respective reaction is rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum has been recognized as the most active catalytic metal towards oxidation of ethanol at low and moderate temperatures. But Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of metal oxo species of tungsten, titanium or zirconium.

We pursue a concept of utilization of mixed metal (e.g. zirconium/tungsten or titanium/tungsten) oxide matrices for supporting and activating noble metal nanoparticles (e.g. PtRu) during electrooxidation of methanol and ethanol. Among important issues is incorporation of Rh nanostructures capable of weakening, or even breaking, the C-C bond in the ethanol molecules. On the other hand, rhodium itself is not directly electrocatalytic toward oxidation of ethanol. The oxides and noble metal nanoparticles have been deposited in a controlled manner using the layer-by-layer method. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account possibility of specific interactions of noble metals with transition metal oxide species as well as existence of active hydroxyl groups in the vicinity of catalytic noble metal sites. In addition, formation of “nanoreactors” where ethanol is partitioned (at Rh) to methanolic residues further oxidized at PtRu cannot be excluded.

We also demonstrated here that deposition of Pt and bimetallic PtRu nanoparticles onto nanostructured zirconia (pristine or admixed with tungsten oxide) support leads to the enhancement of their catalytic activities toward electrooxidation of dimethyl ether (DME). It is reasonable to expect that the ability of oxides to induce acid catalysis (weakening of C-O bond in the ether), increase proton mobility, and to donate active hydroxyl groups at the electrocatalytic interface are responsible for the observed catalytic enhancement effects. Mutual activating interactions between ZrO_2 and platinum or ruthenium components resulting in the formation of sub-stoichiometric oxide and changes in the electronic properties of Pt and Ru are also feasible. The fact, that the onset potential for the oxidation of DME is somewhat shifted toward less positive potentials in the presence of zirconia, is of practical importance.

Microbial Fuel Cell Stack for Treatment and Off-grid Power from Human Urine: Multi-parameter Analysis

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An estimated 4 billion people do not have access to safe-sanitation systems, which is one of the most critical global challenges. Numerous innovations are being pursued for cost-effective and resource-conserving treatment of human waste [1]. The main aim of this study is to demonstrate the production of electricity from human urine in the field, using Microbial Fuel Cells (MFC) and at the same time, analyse the treatment performance in laboratory conditions. The MFC technology is driven by a microbial "engine" in the anode (negative half-cell) that transforms chemical energy of the 'fuel' (urine) directly into electrical current. As long as urine is supplied to the MFCs, the bacteria continuously metabolise urine producing electricity.

This study focuses on the laboratory-based part of the work, carried out at UKZN, Durban, South Africa. Two laboratory-based prototypes were tested, whose performance informed the monitoring and evaluation of the large field demonstration in an informal settlement in Durban. The urine was supplied directly from one of the urinals in the community to the MFC field prototype to power LED lighting in the toilet block (reported in a separate publication). The two laboratory-based prototypes were constructed using two types of unglazed ceramic cylinders (membranes) as follows i) small-cylinder cascade was constructed from 50 mm height cylinders and 66 MFCs (22 units/module), ii) large-cylinder (80 mm height) cascade consisted of a total of 18 MFCs (6 MFCs/module). Anode electrodes were made of carbon veil fibre and cathode electrodes were constructed using activated carbon fitted inside the ceramic cylinders. All MFCs were electrically connected in parallel. Both cascades were fed with human urine collected from the urinal and monitored over a 6-month period for power performance, COD treatment, macro (N,P,K) and micronutrient content, pH and ionic strength.

Power output from the small-cylinder cascade was 13-39 mW, while the large-cylinder cascade was 5-26 mW (Fig 1) which might be due to the increased surface to volume ratio in the small cylinder cascade. The COD removal was up to 45 % (avg. 23%) in the small-cylinder cascade and up to 34 % (avg. 11%) in the large-cylinder cascade. Up to 73 % and 63 % COD removal was recorded in the catholyte extracted from the small and large cascades, respectively. An important feature of *in situ* electrochemical oxidation is the process of electro-filtration of the urine into a purified catholyte [2]. This finding is in agreement with previous studies. The electrochemical activity showed pH and ion separation between the anolyte and the newly formed catholyte in all tested systems as a function of MFC performance.

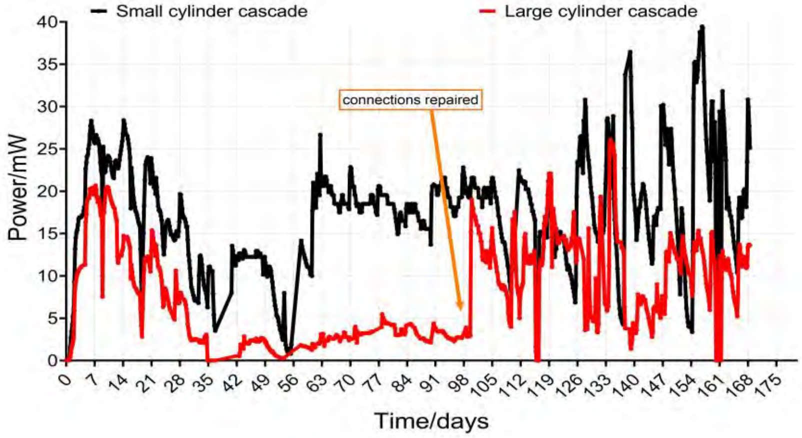

Fig.1 Power performance of small-cylinder and large-cylinder MFC cascades over 6 months.

Opportunities and challenges were identified during the long-term operation of MFC cascades to advance the technology further into self-sustainable sanitation systems and to emphasise the importance of stacked MFC prototypes for the production of off-grid power from human urine with simultaneous treatment.

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When the Whole is better than the Sum: Silver-Titania and Gold-Titania Hybrid Nanomaterials for Electroanalytical Sensors.

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The interest of the scientific community for nanotechnologies and nanomaterials has increased in the last years due to their peculiar characteristics: increased surface / volume ratio, new optical and physical properties, high active surface, increased or modified material transport, increased selectivity. All these features make nanomaterials extremely suitable for a wide range of applications, from energy to catalysis and, last but not least, sensors [1].

Recently, apart from the application of nanomaterials characterized by a single component, the use of "hybrid" nanomaterials, composed of two or more components in "intimate" contact, is also rapidly growing [2]. This is connected to the fact that, since in a hybrid material the establishment of synergistic properties is confined to the contact region between the different components, in nanomaterials, given the small size, these effects can become a dominant factor of the entire structure. The result is precisely the establishment of new and unexpected properties (often desired and interesting) which are not the simple sum of individual contributions. Therefore, hybrid materials are excellent candidates for applications in the most varied fields, including electroanalysis, which can greatly benefit from these systems.

In this context, this work aims to present the construction of devices based on hybrid metal-semiconductor nanomaterials (based on silver or gold nanoparticles and titanium dioxide) [3-5]. In these systems, the presence of metal nanoparticles is exploited for the electroanalytical determination of analytes of medical / diagnostic or environmental interest, while the presence of TiO_2 is essential for overcoming the problems of fouling and passivation of the electrode surface following the determination of the molecule under examination. The possibility of renewing the electrode surface simply by irradiating the device with ultraviolet light, allows to use the devices remotely for a long time, without their continuous recovery [5]. In the case of the Ag-TiO_2 system, an "intimate contact" interphase between the silver nanoparticles and titanium dioxide was also found [6], which makes the hybrid a real new material, with different characteristics and with interesting applications compared to its precursors.

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Composite Nafion Membranes with $CaTiO_{3-\delta}$ Additive for Fuel Cell applications

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Manufacturing ion-conducting membranes with high ionic conductivity and durability is a crucial challenge in the development and large-scale distribution of electrochemical energy conversion devices. Perfluorosulfonic acid polymers are the state-of-the-art solid electrolytes used in low temperature proton exchange membrane (PEM) fuel cells and electrolyzers [1]. Desirable PEMs must be highly proton conductive under hot and dry conditions, thermally and dimensionally stable, impervious to fuels, as well as to electrons.

In the present work, composite membranes based on a Nafion polymer matrix, incorporating a non-stoichiometric calcium titanium oxide ($CaTiO_{3-\delta}$) additive, were synthesized and characterized [2,3].

Fundamental characterizations, by means of thermal and dynamic mechanical analyses, as well as of broadband dielectric spectroscopy, were carried out. Composite electrolytes, containing 5 and 10 wt.% of the $CaTiO_{3-\delta}$ additive, with respect to the dry Nafion content (respectively, M5 and M10), were compared to a plain, additive-free Nafion membrane.

The membrane with the lower amount of additive displayed the highest water affinity and the highest conductivity, indicating that a too-high dose of additive can be detrimental for these particular properties. The mechanical behavior of the composite membranes is similar to that of plain Nafion, slightly improved by the filler addition. These findings indicate that perovskite oxides can be useful as a water-retention and reinforcing additive in proton-exchange membranes for fuel cell applications.

Indeed, the composite membranes developed in this study were evaluated in a DMFC single cell at 30 °C, 60 °C, 90 °C and 110 °C. Interestingly, when the operation temperature is raised to 110°C, the cell adopting M5 composite membrane shows the best electrochemical performance, as a result of the enhanced M5 thermal stability.

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Sustainable electrocatalytic water treatment: Considering the use of earth-abundant materials for nitrate remediation

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Ensuring access to safe water and sanitation is essential to human health, and water quality is an integral part of several United Nations Sustainable Development Goals. One of the utmost concerns is associated to Nitrogen cycle imbalance associated in part to anthropogenic NO_3^- water pollution. Among the nitrate challenges, drinking water with elevated NO_3^- levels is harmful to human health and is associated to respiratory and reproductive system illness, some cancers and thyroid problems. Nitrate pollution is one of the top ten water quality violations reported worldwide [1]. Point-of-use (POU) treatment systems are small treatment units that can remove hazardous pollutants at household level or under your water tap. These types of units should be user-friendly, chemical-free, and avoid waste generation (i.e. brines, biosolids). In this frame, electrocatalytic reduction of nitrate (ERN) is an emerging technology that can selectively reduce NO_3^- to innocuous dinitrogen (N_2). Actually, the current science challenge is how to step at a mid-point oxyanions state, like N_2 rather than NO_2^- or NH_4^+ [2].

Fundamental research on ERN studied the electrocatalytic properties of noble metals and platinoid materials as cathodes. However, these electrocatalytic materials would be the cost driver of POU units and would hinder application and commercialization. Moreover, considering life cycle analysis of the operational life of such endangered elements suggests that their use would be non-sustainable [3]. Therefore, the aim of this paper is to provide a framework for selection of promising earth-abundant elements (carbon-based, cobalt, copper, iron, nickel, titanium, tin, or zinc) that could be used to electrocatalytically degrade nitrate in drinking water to innocuous byproducts using identical conditions. Discussion is sustained in terms of the performed balance considering electroreduction kinetics, selectivity towards nitrogen evolution, electrical energy per order, and material cost/availability. Electrokinetic reduction rates of nitrate using earth-abundant elements were ~1.5-fold faster than Pt (k_1 = 3.7×10-5 s^{-1}). BDD and Sn revealed the highest average selectivity over time towards nitrogen gases evolution (55% and 64%, respectively) and outperformed the Pt electrode which only had 1%. The earth-abundant electrode materials allowed the highest Faradaic efficiencies (10-22%) with electric consumption per order of about 39-49 kWh m^{-3} $order^{-1}$.

These encouraging results highlight the opportunity to apply low-cost materials, which global availability is still not endangered, to nitrate removal. Finally, the use of nanotechnology is a further strategy plan to enhance the competitiveness of these materials.

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First Evidence for Applicability of Microbial Electrochemical Snorkel for Metal Recovery

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The microbial electrochemical snorkel (MES) is a short-circuited microbial fuel cell, which does not produce power but ensures the highest possible electrochemical reaction rates that the system can support. Since proof-of-the principle [1], various possible applications of MES have been reported [2], but not for metal recovery till now. In this study, we provide for the first time evidence for copper recovery performed by MES. A plain copper sheet, immersed in 1 g/L Cu^{2+} solution, was directly connected to an anode of long-term operating sediment microbial fuel cell. In another identical set up a copper cathode and an SMFC anode were connected through a 510 Ω load resistor. The potential of copper electrodes and the current was monitored over time (Fig. 1a), and the concentration of dissolved Cu^{2+} in the catholyte was analyzed by spectrophotometric measurements (Fig. 1b). In the frame of 7 days, 53.1% and 56.3 % copper recovery were achieved for the MES and MFC, respectively. The high extent of copper recovery obtained paves the way for the scale-up of the MES technology for practical application.

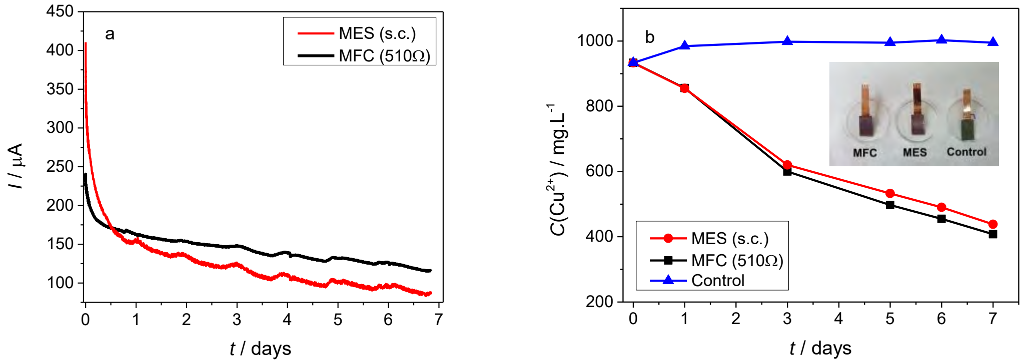

Fig. 1. Changes in: a) current during copper recovery by MES and MFC; b) copper concentration in solution over time.

Acknowledgments: This study was supported by the National Scientific Program "Low-carbon energy for transport and domestic use - EPLUS" (grant agreement D01-214/2018) and implemented in the Integrated Laboratory of the Research Infrastructure "Energy Storage and Hydrogen Energetics" (grant agreement D01-160/2018).

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Modeling Electrochemical CO_2 Reduction Across Scales

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The environment of a CO_2 electroreduction (CO_2ER) catalyst is intimately coupled with the surface reaction energetics and is therefore a critical aspect of the overall system performance. The immediate reaction environment of the electrocatalyst constitutes the electrical double layer (EDL) which extends a few nanometers into the electrolyte and screens the surface charge density. In this talk, we resolve the species concentrations and potential profiles in the EDL of a CO_2ER system by self-consistently solving the migration, diffusion and reaction phenomena using the generalized modified Poisson-Nernst-Planck (GMPNP) equations which include the effect of volume exclusion due to the solvated size of solution species. We demonstrate that the concentration of solvated cations builds at the outer Helmholtz plane (OHP) with increasing applied potential until the steric limit is reached. The formation of the EDL is expected to have important consequences for the transport of the CO_2 molecule to the catalyst surface. The electric field in the EDL diminishes the pH in the first 5 nm from the OHP, with an accumulation of protons and a concomitant depletion of hydroxide ions. This is a considerable departure from the results obtained using reaction-diffusion models where migration is ignored. Finally, we use the GMPNP model to compare the nature of the EDL for different alkali metal cations to show the effect of solvated size and polarization of water on the resultant electric field. Our results establish the significance of the EDL and electrostatic forces in defining the local reaction environment of CO_2 electrocatalysts.

Furthermore, gas diffusion electrode (GDE) based setups have shown promising performance for CO_2 electrocatalysis and further development of these systems will be important on the path to industrial feasibility. To better understand this system, here we model an effective catalyst pore within a flow-cell to study the influence of the catalyst structure and operating conditions on the reaction environment for CO_2 electrocatalysis at practically relevant current densities. We show that the length of the catalyst pore as well as the boundary conditions at the gas-electrolyte and electrolyte-electrolyte interfaces across this length are highly influential parameters for determining the conditions within the catalyst pore. Properties such as electrolyte pH and buffer breakdown, ionic strength and CO_2 concentration are sensitive to the catalyst layer thickness, gas pressure, electrolyte flow rate and the flow-channel geometry. The applied potential impacts the concentration of ionic species in the pore, which in turn determines the solubility of CO_2 available for the reaction. Our results underline the need to understand and manage transport within GDE-based electrocatalysis systems as an essential means to control catalyst performance. Benchmarking of GDE-based electrocatalytic systems against their structural and operational parameters will be important for achieving improvements in performance that can be ultimately translated to large-scale operation.

Semiconducting Transition Metal Dichalcogenide 2D Nanoflakes for Photoelectrochemical Applications

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Given their established robustness and favorable optoelectronic properties, the layered semiconducting transition metal dichalcogenides (TMDs, e.g. MoS_2 and WSe_2) are attractive for optoelectronic applications including photoelectrochemical solar fuel production.[1] Recent advances in the liquid-phase exfoliation (LPE) of semiconducting TMDs into mono- or few-layered 2D nanoflake dispersions and their processing by inexpensive roll-to-roll techniques suggests that large-area TMD-based devices can be fabricated scalably and at low cost.[2] However, the high concentration of defects in these materials act as recombination sites for photogenerated carriers and limit their performance. In this presentation the challenges with charge transport, separation, recombination, and interfacial transfer in LPE TMD nanoflake thin film devices will be discussed with respect to the 2D flake size and defect passivation/charge extraction treatments.[3] Our results give insight into the roles of both edge and internal defects and suggest routes for improvement. Overall it is shown that LPE semiconducting TMDs with suitable defect mitigation can achieve internal quantum efficiency for photon harvesting similar to bulk single crystal samples. Specifically, we show that WSe_2 nanoflake thin films achieve absorbed-photon-to-current efficiency over 50% and photocurrent densities for solar water reduction at 4 mA cm^{-2} under standard testing conditions.[4] These results suggest that roll-to-roll processed 2D WSe2 may be a suitable photocathode for economical solar-to-hydrogen conversion with a photoelectrochemical tandem cell. The role of the exfoliation methodology on the formation of defects and a path towards further performance enhancement (including increasing the photopotential of the TMD photocathodes), are also discussed.

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Electrochemical Insights of Multilayer CVD Graphene Decorated with Colloidal TiO_2 Nanocrystals for electroanalytical applications

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Optically transparent and UV-light photoactive hybrids based on TiO_2 nanocrystals (NCs) surface modified graphene, were synthesized by a direct and facile solution-based procedure. Graphene was grown by Chemical Vapor Deposition (CVD) and transfered on ITO coated glass substrate as single- or multilayer (up to file layers) films., TiO_2 NCs synthesized by a chemistry colloidal route and surface functionalized by 1-pyrene butyric acid (PBA) by a capping exchange procedure [1], were anchored onto the graphene films thanks to π-π interactions.

SEM, EDS, AFM and Raman spectroscopy were conducted to physico-chemically characterize the materials. It was verified the successful immobilization of the colloidal NCs onto the graphene films, which preserves and concomitantly enhances the graphene intrinsic structural properties. In particular, we observed an electrical conductivity higher than that measured for the bare graphene films, which has been accounted for by a p-doping effect, due to a hole transfers from the nano-objects to graphene, mediated by the short aromatic ligand acting as charge channel.

Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were then employed to complete and enrich the characterization of the hybrids. It was observed that the hybrids-properties are strongly dependent on the number of layers of the CVD graphene. The use of two redox mediator probes, namely the inner-sphere, surface sensitive ($K_4Fe(CN)_6$) and the outer-sphere, surface insensitive ($Ru(NH_3)_6Cl_3$), allowed understanding these features from a morphological point of view. The results showed a strong difference between the mono-, the bi- and the other multi-layers, in terms of different diffusional mechanism and redox active sites [2-4].

Moreover, the stacked layers of the pyrene-coated TiO_2 NCs are found to increase the electroactivity, the capacitive behavior, as well as the photo-electrical response of graphene, concomitantly maintaining its high charge mobility.

For all the above reasons, the described hybrids have a great potential as optically transparent components for manufacturing photoanodes to be integrated in (photo)electrochemical sensors, as well as solar cells or photodetectors and in FETs.

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Development of denitrifying bio-cathodes and study of their bacterial communities

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One consequence of intensive agriculture is pollution of natural waters by nitrate. At high concentration nitrate coupled with phosphate pollution triggers eutrophication and green algae bloom in the environment. One possible application of microbial electrochemical technology is the stimulation of denitrification in natural waters. In 2007, the first denitrifying bio-electrochemical system (BES) was reported.[1]

In this study, denitrifying bio-cathodes with specific design were developed under constant polarization during incubation in natural sediments and water supplemented in nitrate at different time. The electrodes were built using stainless-steel with three different separated compartments for each electrode in which graphite granules were added and also polarized (cf. figure 1). The goal of this design is to see a possible difference in bacterial communities depending on the compartment the graphite granules were collected, the first compartment being buried in sediments, the second being half in water and half in sediments and the third being totally in water. To compare the efficiency of the bio-cathodes and to increase the reliability of the global experiment, six pilots were launched, three with the same polarized electrodes and three without as negative controls.

Results collected during the incubation show both an electrochemical response to nitrate addition on chronoamperometry for two of the pilots with electrodes and a noteworthy increase of nitrate removal for all the three pilots with electrodes although the increase, in the case of the third pilot showing no electrochemical response to nitrate, remains lower compared to the two others.

This third electrode showing no electrochemical response to nitrate addition became an interesting tool of comparison for the 16S rRNA study, making possible to compare the bacterial communities between the two electrodes sensitive to nitrate on chronoamperometry and this last one in order to have a more precise idea of the strains involved in bio-electro-chemical denitrification.

After 27 days of incubation under polarization, the three electrodes were dismantled and the graphite granules from the three compartments of each electrodes were submitted to DNA extraction protocol and sent to 16S rRNA sequencing. The first noticeable result was a higher abundance of the Proteobacteria group in the middle compartment (half in sediments, half in water), this group being known in literature to contain a large proportion of the identified electroactive denitrifying species[2]. After a closer look at microbial communities on the middle compartment of each electrodes, it is possible discern noticeable differences between the two electrochemical nitrate responding electrodes and the last one showing no reaction to nitrate addition on chronoamperometry.

The most interesting difference is the presence of a specific bacterial species named Azoarcus spp. in the middle compartment of the two first electrodes responding to nitrate (20 and 15% of relative abundance) and its near absence in the middle compartment of the third, indicating that this specie could be involved in the electroactive denitrification, *Azoarcus spp.* being already identified in many MFC but not yet characterized as electroactive[3].

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Electrochemical Reduction of Substituted Nosylamidic Intermediate – Precursors of New Anionic Receptors

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Anions play an important role in biological systems. At the same time, many of them are the major environmental pollutants and substances endangering living organisms. Anion recognition, elimination and sensing would find application in many areas including medicinal or environmental chemistry. Suitable examples of anionic pollutants are phosphates, which could cause eutrophication of water and they are also known for their limited removal from body fluids, which could lead to serious health problems. Therefore, the aim of our research group is the design and preparation of new anionic receptors with suitable binding sites to bind these anions.

In the first step of our synthesis we prepared a series of substituted nosylamides (fig. 1a, b). These substances are suitable intermediates in the synthesis of novel receptors bearing ureido functions. The sulfonamide motif is known from the literature as a neutral hydrogen bond donor. Therefore the main question in this study was the role of the sulphonamidic hydrogen, its acidity in correlation with the structure and substitution of the whole molecule. For better understanding and for "tuning" of the behavior of the final urea receptors, the properties of these intermediates were studied electrochemically using polarography and cyclic voltammetry with mercury drop electrodes in dimethylformamide with $Bu_4N\ PF_6$ as electrolyte, and by various spectroscopic methods.

The nitro groups in our intermediate molecules are not only important substituents enabling continuation in synthesis, but also electrochemical "probes" reflecting the electron properties of the parent molecule. Their reduction in aprotic media is generally known: after the first one-electron reversible reduction step where a stable radical anion is formed, a three-electron irreversible process follows resulting in the corresponding hydroxylamine.

Whereas the electroreduction of the series 1a (as models) occurs according to the expected pattern and the observed potential shifts follow the influence of the *p*-substituted R according to the linear free-energy relationship (LFER) of the Hammett type [1-2], the reduction pattern of the series 1b is entirely different: After the first irreversible step (theoretically involving 4/5 of electron) a one-electron reversible reduction takes place followed by a multielectron process. This behavior corresponds to the autoprotonation mechanism [3] where the acidic hydrogen of the amidic group is involved. In this way, the influence of substitution on acidity is followed.

Figure 1 **a** **b**

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Photobioelectrode Based on 3D Reduced Graphene Oxide and Photosystem I

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Technical advances in materials chemistry enable many new possibilities in electrochemistry. This is especially helpful in biohybrid systems. A very broad range of tunable surface characteristics is essential to adapt the electrode to the specifics of the biomolecules. These developments are relevant to all sorts of semi artificial systems, e. g. in the field of bioenergy.

Photobioelectrodes, which use photoactive protein complexes to convert light into current and valuable chemicals, are a comparatively recent field of research.[1] The goal of this work is the buildup of a photobioelectrode based on 3D graphene and photosystem I (PSI). Here a facile, scalable approach was targeted. The construction was realized by using reduced graphene oxide, which is relative cheap and accessible on a larger scale.[2] A 3D structure is generated by a template procedure based on latex beads and spin coating. The general template approach already proved to be successful for photobioelectrodes made of other materials.[3] Different reduction methods were tested and a hydrazine treatment was optimized for the constructed material.

The obtained electrode has been evaluated regarding the interaction with PSI. An assembly as well as the direct electron transfer from electrode to the reaction center is ensured resulting in a cathodic photocurrent. As this communication is not effective, the redox protein cytochrome c is added to connect more PSI complexes. To improve the interaction of the electrode and the proteins different surface modifications have been tested. These experiments indicate that the photocurrent can be further enhanced. The photobioelectrode is characterized with different electrochemical methods such as cyclic voltammetry, chopped light voltammetry and photoaction spectroscopy. Additionally, analytical methods such as UV/VIS spectroscopy and scanning electron microscopy (SEM) have been applied. It is noteworthy that the thickness of the electrode material is adjustable in the manufacturing process. Even by preparing multiple layers the final electrode remains transparent, which is advantageous as it is therefore still suitable as photobioelectrode.

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Three-Dimensional Nanoparticle Structure, Surface Area and Activity

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The characterization of nanomaterials is a key aspect of determining if the behavior and/or properties of a 'new' material differs from that of its bulk counterpart. However, determining structure at the nanoscale remains a challenging problem. This issue is compounded for platinum group based materials due to the tendency for them to form larger irregular structures. For platinum nanomaterials, aggregation-based crystal growth is an important synthetic pathway. In this case seed particle coalescence leads to the production of larger semi-disordered mesoporous structures. In order to study the possible catalytic activity an electroanalytical utility of these materials we need to fully characterize their atomic structure and surface areas. This presentation starts by showcasing some advanced transmission electron microscopy techniques, such as tomography (Fig. 1) and quantitative 2D image analysis, and demonstrating to what extent these tools can give us insight in the internal structure of the nanomaterial. Building on work focused on the measurement of single nanoparticle surface areas[1,2], two example catalytic reactions are studied[3,4] and the rate shown to directly reflect the measured surface area of the material, validating and demonstrating the use of this single nanoparticle electrochemical technique.

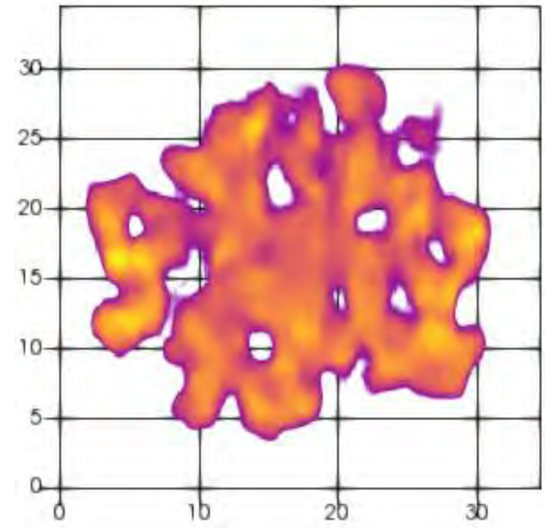

Figure 1: Reconstructed tomographic slice through a ca. 30nm mesoporous platinum nanoparticle, showing the internal structure of the nanomaterial. Image provided by and with thanks to Y. Wang and S. Haigh of Manchester University, UK.

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EPR-Spectroelectrochemical Study of *cone*-Calix[4]arene nosylates

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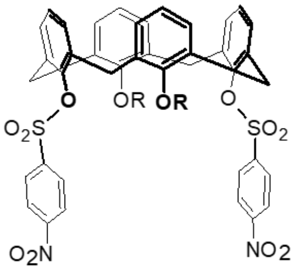
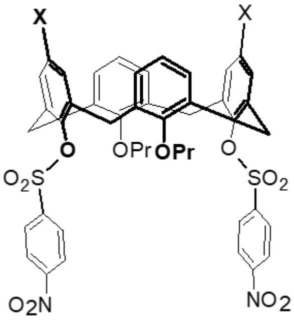
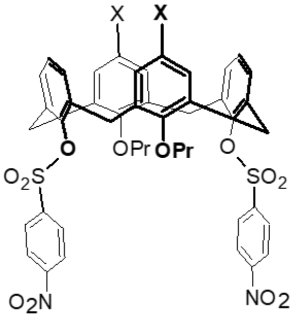
Calix[4]arene nosylates are important intermediates during preparation of ureidocalix[4]arene-based anion receptors, double calix[4]arene derivatives for fluorescent applications, self-assembled calixarene nanotubes or calixarene based molecular capsules.



1: R = CH_3
2: R = $CH_3CH_2CH_2$



3: X = CHO
4: X = CH_2OH
5: X = CH=NOH



6: X = CHO
7: X = $CH(SCH_2CH_3)_2$

Series of seven cone-calix[4]arene sulphonates substituted by various groups (nitro, carbonyl, oxime and other) was investigated in terms of their electrochemical reduction mechanisms. The experimental study includes both DC-polarography and cyclic voltammetry results combined with in situ EPR-spectroelectrochemistry in aprotic DMF.

All the investigated aryl nosylates are reduced in three steps. First electron(s) reduce(s) the molecule reversibly under formation of nitro anion radicals. In case of calixarenes, both nitro groups are reduced simultaneously, which refers to their independency. No or only negligible mutual electronic interaction of both nitro radical centres is confirmed by well resolved hyperfine EPR spectra structure. In the following step, two electrons per one nitro group are accepted, which leads to splitting of the S−O bond, and therefore to formation of phenols and nitro substituted arylsulphinates. The interpretation is based on (i) EPR-spectroelectrochemical measurements (comparison of the EPR-spectra with standards), (ii) DC-polarography and cyclic voltammetry (comparison of the reduction potentials with standards), and finally supported by quantum chemical calculations (identification of the thermodynamically most favourable reaction pathway). At more negative potentials, all nitro anion radicals are reduced (with assistance of protons present in the solution from moisture) by next three electrons to corresponding hydroxylamines.

This work wass supported by Grant No. 18-12150S (Grant Agency of the Czech Republic) with the institutional support RVO: 61388955. Access to computing and storage facilities owned by parties and projects contributing to the National Grid Infrastructure MetaCentrum provided under the programme "Projects of Large Research, Development, and Innovations Infrastructures" (CESNET LM2015042), is greatly appreciated.

Design of an electrochemically gated organic semiconductor for pH sensing

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Since the development of potentiometric ion-selective electrodes, remarkable steps have been taken towards progressive simplification and improved robustness of pH sensing probes. In particular, the design of compact sensing architectures using solid-state components holds great potential for portable and wearable applications. In this scenario, the use of organic electrochemical transistors (OECTs) to fabricate referenceless sensors with potentiometric transduction has been recently reported by our group [1]. Moreover, an innovative gateless (i.e. two-terminal only) configuration has been proposed for Chloride sensing based spontaneous electrochemical gating [2].

In this contribution we report the development of an electrochemically gated device for pH sensing, combining the robustness of potentiometric-like transduction with an extremely simple and integrated geometry requiring no reference electrode [3]. The sensor is a two-point probe device comprising two thin polymeric films, i.e. a charge transport layer based on poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and a pH-sensitive layer. The latter is based on the Nernstian transducer PEDOT:Bromothymol Blue (PEDOT:BTB) [4]. The transduction mechanism originating the sensitivity to pH variations is thoroughly discussed to introduce the concept of spontaneous electrochemical gating.

The two-terminal pH sensor reported here shows remarkable potential for sensor miniaturisation and the development of portable and wearable electrochemical probes. Indeed, the chemiresistor-like geometry based on flexible, all-polymeric materials is compatible with photolithography-free, high throughput and low-cost fabrication techniques, such as screen-printing, and adapts to conformable substrates with potential integration into clothes or other real-life objects. To prove the versatility of our architecture, we fabricated a two-terminal sensor on a bioceramic fabric for real-time pH monitoring (Figure 1).

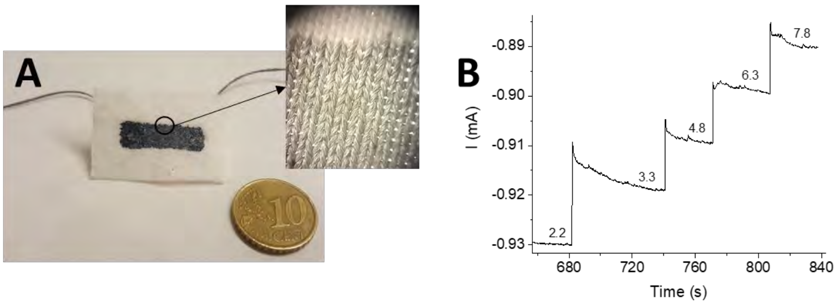

Figure 1. (**A**) Photo of the two-terminal wearable sensor. (**B**) Current vs time response to pH variations in Universal Buffer following 1M KOH additions obtained with the textile sensor. V_{app} = -200 mV.

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Combating self-corrosion of Mg anodes via synergistic inhibition

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Mg-air primary battery recently become more and more attractive for special applications thanks to their environmental benignity, economic viability, and high theoretical specific power density. However, the high tendency to self-corrosion of Mg-based anodes and their fouling during discharge lead to relatively low specific energy efficiency.
This work reports the strategy on decreasing the self-corrosion of Mg anodes via microalloying with Ca and design of the electrolyte additives in order to improve the energy efficiency of Mg-air batteries.

It was shown previously [1], addition of Fe^{3+} complexing agents into electrolyte significantly inhibits parasitic self-corrosion and improves the Mg behaviour under anodic polarization [2]. However, in many cases, hydrogen evolution reaction is not completely suppressed. The relevant method to thoroughly control hydrogen evolution reaction is to use combination of different inhibitors. Herein we combined Fe^{3+}-complexing agents, that prevent detrimental iron re-deposition, with efficient magnesium inhibitors (sodium nitrate and nitrite) that reduce parasitic hydrogen evolution reaction. The combination of inhibitors was chosen based on knowledge of magnesium corrosion mechanism and experience with corrosion inhibitors of Mg. In this work the effect of single additives and their combination was studied. Additionally, localised measurements of pH and dissolved oxygen above magnesium surface during polarisation were done in order to give insights on the inhibition mechanism. The results show that use of combination of inhibitors reduce significantly the self-corrosion and in addition prevent formation of $Mg(OH)_2$. The most effective was the mixture of sodium salicylate-sodium nitrate. This work is a step further to the improvement of the Mg-air battery performance.

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Porous Carbons Derived from Alcohol-Treated Bacterial Cellulose for Li-O_2 Batteries

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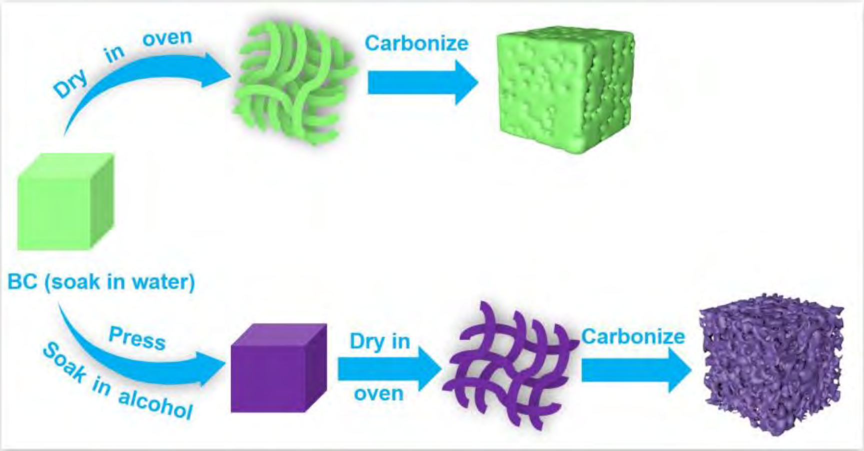
Porous carbons are important cathodes for Li-O_2 batteries. But most ways of preparing porous carbons are high cost and complex. We present a simple and low-cost route to prepare porous carbons from food-grade bacterial cellulose (BC). By carbonizing as-prepared aqueous hydrogel BC, usually the porosity of the nanofibre network is lost because of its partial melting, and a compact carbon is obtained. Porous carbons can be obtained when using alcohols to treat BCs. And the carbon resulted from 1-butanol treated BC possesses outstanding discharge capacity and good cycle life for Li-O_2 batteries. This work presents a tunable, cost-effective and scalable method for obtaining porous carbons from sustainable sources.



Acknowledgements
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Constructed Wetland-Microbial Electrochemical Snorkel system for efficient denitrification

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The exceeded nitrate concentration in surface waters is caused by the use of nitrogen fertilizers in agriculture and may bring several negative consequences, e.g. excessive eutrophication. One solution for remediation is to collect water draining from the fields in constructed wetlands (CW), in which nitrate can be used as terminal electron acceptor by bacteria present in the sediment. However, size of the wetland is often not sufficient for efficient treatment of the watershed, when the highest nitrate concentrations are observed.

Microbial Electrochemical Snorkel (MES)[1] is a simplified version of Microbial Fuel Cell in which anode and cathode are short-circuited. The anodic part of the system reacts with electron donors (organic and inorganic compounds) and the cathodic part reacts with electron acceptors (oxygen and nitrate) but no energy is produced by the device. The main advantage of MES is to maximize the current flowing between anodic and cathodic parts for a more efficient water treatment.

Currently, we are investigating MES in a constructed wetland with the aim to increase the denitrification rate. Stainless steel and graphite felt have been used as electrode material to build MESs which were compared with control experiments in wetland without any electrodes. After optimization of the device, a significant improvement was achieved as it is illustrated on Figure 1. These series of experiment were performed in triplicate with an initial nitrate concentration in the range of 33 to 40 mg $N\text{-}NO_3^-$/l. The best fit to adjust the model to experimental data was obtained by considering an apparent first order reaction with $C = C_0e^{-kt}$.

Here, we achieved k values for the CW-MES (0.117 ± 0.012 hour^{-1}) that are five times higher than the control experiment with CW only (0.022 ± 0.002 hour^{-1}). We are now investigating the electromicrobial mechanisms that allows such large increase in denitrification rate and we started evaluating on-field applications. This communication will summarize our latest results about denitrification with microbial electrochemical systems in constructed wetlands.

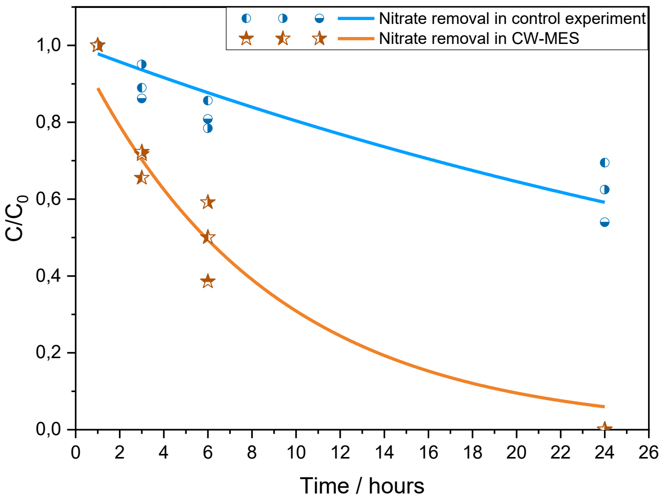

Figure 1 Experimental points and adjusted model of nitrate removal in CW-MES and control

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Acknowledgements: financial support from The French National Research Agency (ANR-17-CE04-0004) is gratefully acknowledged.

Electrochemistry of Luminescent Cationic Group 4 Metallocene Complexes Stabilized by Pendant N-donor Groups

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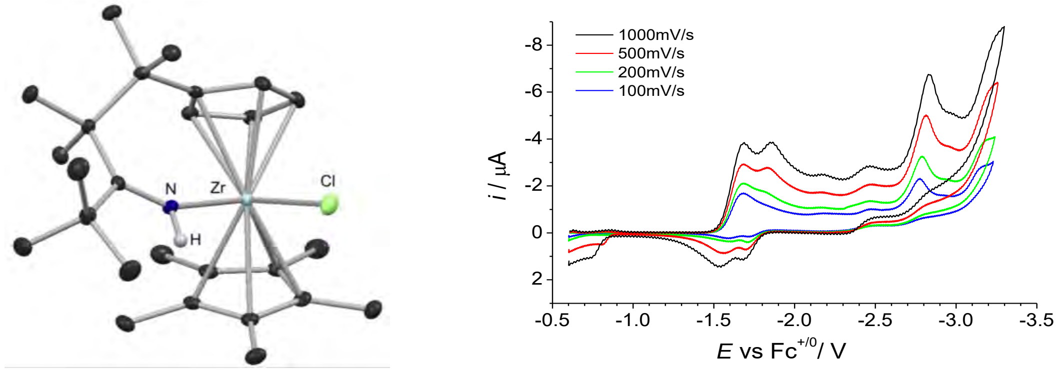
Photoluminescent metal complexes have a broad application potential in various fields such as photocatalysis, photovoltaics, light-emitting devices, molecular sensors, bioimaging, etc., but among them the complexes of electron-deficient metals with LMCT excited states are rather scarce. We have observed phosphorescence of a new class of Zr and Hf metallocene complexes with intramolecularly tethered imine or pyridine moiety (obtained by protonation of the ketimide group or abstraction of chloride anion in parent neutral complexes [1,2]) both in the solid state and in solution at ambient temperature with relatively high quantum yields and luminescence lifetimes up to tens of µs.[3]

Because charge transfer in photochemistry and electron transfer in electrochemistry are in close relationship, and because redox stability is a very important property in this case, electrochemical methods are inevitable in this research. In order to understand the energetic as well as kinetic relationship between various excited states and redox states, a series of cationic 4 metallocene complexes (Ti, Zr, Hf) stabilized by pendant N-donor groups was synthesized and studied by electrochemical methods.

In the accessible potential range all studied compounds involved several reduction steps, suggesting a complicated mechanism. Almost all derivatives are reversible reduced in the first step. The influence of metal atom and the substitution of the ketimide or pyridine moiety on the potential is discussed. The results are compared with DFT calculations.



left – A solid-state structure of cationic zirconocene with coordinated imine moiety; the $[B(C_6F_5)_4]^-$ *anion is omitted for clarity; right – The scan rate dependence of cationic zirconocene with coordinated imine moiety in THF on mercury electrode.*

The authors thank project 19-00204S (GAČR) for financial support.

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Electrodeposition of semiconductors on silver and silicon substrate through E-ALD and bulk methods

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Semiconductors are commonly prepared using element at high temperature, in vapour phase and high vacuum conditions. Liquid solution using water, organic solvents, or ionic liquids are other possibilities to grow materials in the bulk form or as thin films. Electrodeposition can be performed with simple conditions, at room temperature and ambient pressure saving energy, money and performing green synthesis. Moreover, the electrodeposition can be easily scaled up from a small electrochemical cell to industrial level.

Today electrochemistry plays a crucial role in the material science thanks to methods that permits to control the deposition at atomic level, exploiting surface limited reactions like the underpotential deposition (UPD). The UPD is a well-known phenomenon but recently there is a renewed interest on it because of the possible applications in many technological fields from electrocatalysis (like water splitting) to thin film photovoltaic, display and LEDs, light detectors and lasers. Based on UPD process, it is possible to perform the electrochemical atomic layer epitaxy (ECALE), or E-ALD when the deposits cannot be rigorously considered epitaxial, alternating the deposition of a metal and of a non-metal element in a cycle. With the E-ALD it is possible to avoid the formation of three-dimensional crystallites and Stranski-Krastanov growth. Therefore E-ALD is a valid approach to obtain semiconductors on metallic substrate. In our laboratory, with this method, we successfully synthesized thin films of various 12-16 groups semiconductor compounds like ZnS, CdS, CdSe, CdTe, but also Cu_2S, $MoSe_2$ and Bi_2Se_3 on silver electrode [1,2].

Moreover, we explored also the possibility to performing controlled electrodeposition on silicon. Despite its diffusion in the microelectronic industry, the realization of Si-based devices is extremely challenging due to its indirect bandgap and a suitable candidate to integrate light in silicon and open the microelectronic world to the light remains to be found. Among semiconductors, other materials are emerging to face the important demand to produce novel optoelectronic devices integrated in Si platforms. The possibility of integrating various materials on the Si surface offers the opportunity to produce compact and cost-effective electronic circuits with numerous applications. Finding UPD conditions on Si is extremely difficult but operating in severe regimes of charge and time-controlled deposition it is possible to obtain an E-ALD-like deposit [3].

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Redox charge storage in two-dimensional transition metal carbides (MXenes)

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Two-dimensional (2D) transition metal carbides known as MXenes, have received considerable attention for energy storage applications due to their tunable electronic and physical properties.[1-2] MXenes have high specific capacitances due to their redox-active transition metal surfaces, and binder-free MXene films have electronic conductivities much higher than typical supercapacitor materials (>1000 S/cm compared to <0.1 S/cm).[3-4] Furthermore, MXenes are capable of storing charge in a wide variety of aqueous electrolytes and it has been shown that MXenes are capable of electrochemically intercalating cations of various charges (K^+, Na^+, Mg^{2+}, Al^{3+}) into the interlayer spaces between their 2D nanosheets.[5-6]

There is increasing interest in researching materials with nanoconfined fluids for electrochemical energy storage applications due to the interesting modifications confined fluids can have on ion transport, ion desolvation and insertion, or solvent co-intercalation into host materials. Furthermore, layered materials with these confined fluids can demonstrate higher rates of charge storage and transfer due to decreases in the activation energy of charge-transfer at their solvated surfaces.[7] Since the surface of the MXenes has abundant surface functional groups (e.g., O, F, and OH), surface redox reactions with intercalated protons result in very high volumetric capacitance in acidic aqueous electrolytes. The high electronic conductivity and the water confined within the MXene nanosheets in this system also enables ion transport rates that are far superior to any other known pseudocapacitive material.[4] In organic electrolytes, simply changing the solvent of the electrolyte can dramatically alter the mechanism by which charge storing ions are intercalated into the MXene structure, resulting in significant changes in the amount of charge stored and the mobility of the intercalated ions.[8]

Different MXenes have been synthesized with a large variety of surface chemistries, many of which have demonstrated promising properties for energy storage applications. By further selecting the proper combination between ions, polarization conditions, and the type of MXene, the changeable interlayer space may allow for tunable ion intercalation and improved supercapacitor performance.

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Electrochemical pH sensor for continuous monitoring in minimal invasive device

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pH sensor is used in various applications utilizing redox reactions, encompassing both research and industrial fields. pH plays a significant role in multiple biological processes, like cell proliferation, endocytosis, ion transport and is also a factor in cardiopulmonary and neurodegenerative diseases, including cancer [1]. Minimally invasive techniques enable diagnostics and surgery to be performed through a small incision reducing the damage to healthy tissue leading to faster recovery times for the patient.

Iridium Oxide (IrOx) is one of the electrochemical materials for display devices [2], a popular alternative to conventional glass and other metal-oxide electrodes. Advantages of IrOx sensors include fast response time, reduced chemical interference, and long-term stability, furthermore, these electrodes exhibit functionality at temperatures up to 250°C, high pressures, in hydrofluoric acid, and in non-aqueous solutions [3]. When considering practical applications, the properties of IrOx are very sensitive to structure and composition, which are dependent on fabrication methods and conditions used [4]. Thus, the different characteristics of IrOx pH electrodes are mainly accounted for by different preparation methods.

A pH sensor was developed involving electrodeposition of IrOx films onto platinum films. Anodically electrodeposition of IrOx film were deposited on the electrode via standard electrochemical cyclic voltammetry using a three-electrode setup (Figure 1A). The number of cycles that are carried out corresponds to the level of deposition of IrOx on the electrode surface. Open-circuit potential measurements were performed to evaluate the potential electrode pH response at room temperature using a 2-electrode cell. Comparison of different working electrodes on the same chip and in different chips was carried out (Figure 1B). The sensors showed an excellent reproducibility with a linear super-Nernstian response around 69mV/pH unit in a wide pH range (pH 4−10). The present pH sensor includes excellent adhesion of the pH sensitive layer to the substrate and excellent reproducibility of sensor fabrication, which can lead to a new generation of diagnostic tools for the simultaneous detection of various biological analytes.

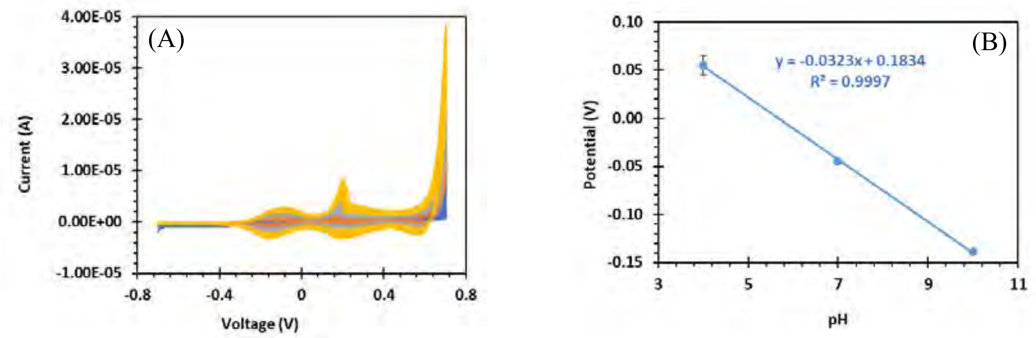

Figure 1: (A) Synthesis of IrOx on Pt microdiscs array (20 cycles were performed with a scan rate of 50 mV/s and a quiet time of 60sec); (B) Calibrations curve of different pH's buffers.

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Room Temperature Electrodeposition of Titanium sub-oxides on Mild Steel Electrode towards Corrosion Protection

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Titanium sub-oxides are mixed-valence compounds containing Ti^{3+} and Ti^{4+} ions, which provides several possible configurations in the crystal. The oxygen vacancies of the Ti-O system have important effects on interfacial electronic structures. Such compounds are also known as Ti_nO_{2n-1} (Ti_3O_5, Ti_4O_7, Ti_5O_9, Ti_6O_{11}, etc.), where $2 < n < 10$. Depending on the n value, their crystal structure, electronic structure, and color can change. In recent years, they have attracted considerable attention due to their excellent properties such as high electrical conductivity, remarkably visible light absorptivity, and chemical stability in aggressive alkali and acidic media. These properties make them suitable for a variety of applications such as cathodic protection, electrode materials, batteries, catalytic support for fuel cells, degradation of pollutants, and electronic and optoelectronic devices [1-3].

In this study, a rapid and simple electrochemical process without a calcination step to prepare titanium sub-oxide coating on mild steel (MS) surface is presented for the first time. The low-temperature synthesis of titanium sub-oxide is carried out on the MS electrode by cyclic voltammetry in acetonitrile solution containing titanyl perchlorate. The coatings obtained various potential intervals and cycle numbers are investigated by comparing with each other using EIS. According to the obtained resistances, the optimum experimental parameter is a potential range of 0.0 V and -2.2 V with 20 cycles. The broad reduction peak at about -1.9 V in the blank solution indicates the formation of Ti_nO_{2n-1} (Fig.1A). The morphology and chemical composition of the coating are studied by SEM-EDX, XRD, and XPS. XRD result indicates the presence of different oxygen-containing phases (Ti_3O_5, Ti_4O_7, and Ti_5O_9) together with Fe_2TiO_5 intermetallic phase. From XPS, the Ti(III) and Ti(IV) oxidation states are demonstrated in the electrodeposited Ti_nO_{2n-1} film on MS (Fig.1B). Corrosion performance of the Ti_nO_{2n-1} coated MS electrode is investigated using EIS, OCP, and Tafel measurements in 0.5 M H_2SO_4. It is determined that the resulting coating, synthesized in a solution containing $TiOClO_4.6H_2O$ on the MS electrode, provides five times more protection in 0.5 M H_2SO_4 medium. The results demonstrate that the electrodeposited Ti_nO_{2n-1} film on MS is a good alternative for practical application of metal-oxide based corrosion systems.

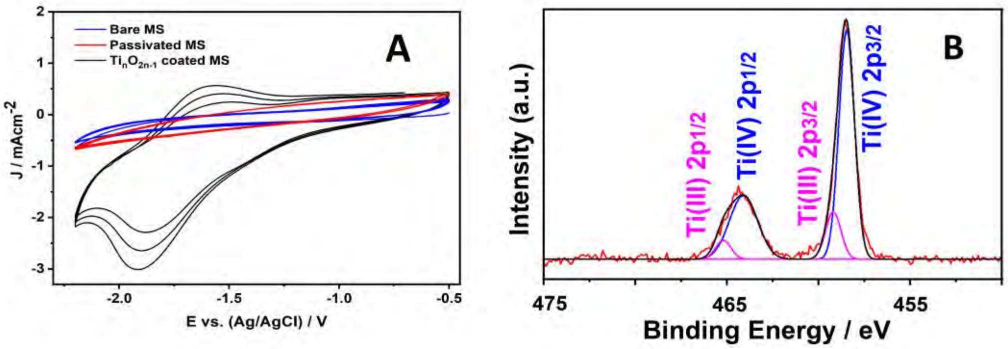

Fig.1. A. Cyclic voltammogram recorded in blank solution (TBAP/ACN) for **(a)** bare MS electrode; MS electrodes coated in TBAP/ACN solution in the **(a)** absence and **(b)** presence of $TiO(ClO_4)_2$, v=100 mVs^{-1}. c_{TBAP} = 0.05 M **B.** Ti 2p XPS spectrum of Ti_nO_{2n-1} coating.

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Pyrene-Cyclobutene Conjugates – Spectro-electrochemical Study of Redox Mechanism

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Conjugated aromatic systems are commonly used for organic electronics as “green smart molecules” free of any metal. Specific properties of these molecules are simply adjustable by chemical modification. Our project is focused on molecules comprising pyrene derivatives and/or other aromatics in combination with cyclobutene representing the tetrasubstituted double-bond bridge. Modifications and conjugations of mentioned molecules result in various extent of electron delocalization. Electrochemical data of pyrene, cyclobuten and their conjugates are essential for understanding the redox mechanism of these large delocalized systems.

Redox mechanism of conjugates was studied in non-aqueous aprotic solutions (acetonitrile and dimethylformamide) at mercury and glassy carbon working electrodes by means of polarography, voltammetry at rotating disc electrode (glassy carbon) and cyclic voltammetry at hanging mercury drop electrode and stationary glassy-carbon electrode. Electron paramagnetic resonance with *in situ* electrochemical generation at platinum working electrode in dimethylformamide was used for detection and characterization of primary and secondary radical intermediates.

Studied systems involved three types of reduction mechanism: I. pyrene with substituents exhibiting induction/mesomeric effect, II. pyrene in combination with other independent reducible centre, III. cyclobutene conjugates with substituents extending the delocalized system (pyrene and/ or other aromatics).

The reduction process of all studied compounds is not "electrode assisted" (mercury, glassy carbon). Potentials in DMF are systematically shifted to less negative values with respect to acetonitrile by approx. 70 mV. The reversibility is more pronounced in DMF, which means that the primary radical anions exhibit higher stability. During oxidation at glassy-carbon electrode, polymerization of pyrene and/or other components was observed.

Pyrene is reduced in two one-electron steps – first to a stable radical anion and subsequently to unstable dianion. Substituents shift the reduction potential in agreement with induction/mesomeric effect.
Direct interconnection of two pyrene molecules by a single bond results in twisted molecule with limited pyrene interaction, proved by formation of stable radical anions.
The cyclobutene bridge enters in conjugation with aromatic substituents (pyrene, tolyl or anisyl) extending planar delocalized system, which was confirmed by partial reversibility of its first reduction step to unstable radical. In the next step, cyclobutene is reduced by simple reduction to cyclobutane (proved by analysis of products of preparative electrolysis by NMR – MS), although the ring opening and splitting of the CH_2–CH_2 bond by the ECE mechanism was suggested in the literature [1, 2].

Pyrene derivatives are good chromophores and redox centres and studied molecules are suitable for construction of organic semiconductor materials. Analysis and interpretation of spectro-electrochemical data of pyrene derivatives and conjugates revealed intramolecular communication of electrons and redox mechanism of conjugates. This knowledge is basic for tuning the required redox properties by chemical modification.

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Three-Way Interactions of Two-Dimensional Crystals

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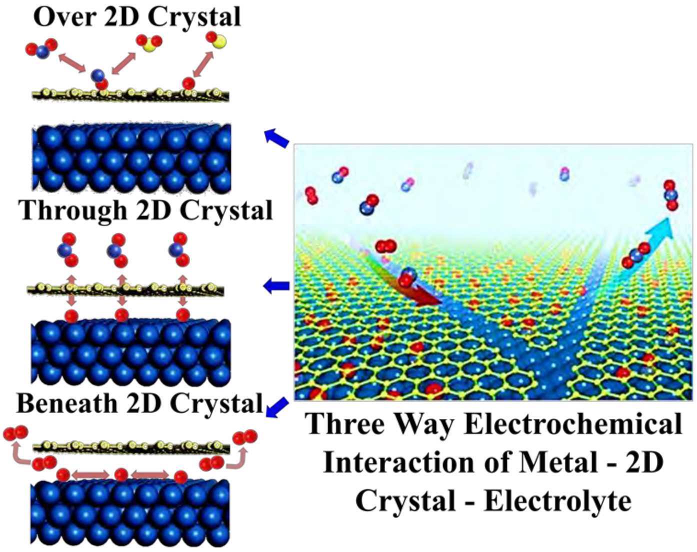
Graphene and related two-dimensional (2D) crystals, a new class of advanced materials, not only improves the performance of the current technological devices but also create new disruptive technologies[1]. From the interfacial electrochemistry's perspective, 2D crystals possess a porous double-sided surface and its integration into a device can lead to multiple interactions namely: i) an electrochemical interaction between the 2D crystal and the electrolyte[2]. ii) The protons (in the case of pristine 2D crystal[3]) or ions (in the case of defect-engineered 2D crystal[4]) permeation through the lattice of 2D crystals. iii) A confined electrochemical interaction in-between the region of 2D crystal and the conducting metal substrate[5].The three-way electrochemical interaction of 2D crystals makes it a unique material and performance tuning of these interactions can radically transform electrochemistry-based technologies.



Therefore, the primary goal of the talk is to present a detailed analysis of a model metal – 2D material – solution interface, i.e. Pt(111) – graphene – electrolyte interface[6], with an objective to emphasize and define the fundamental aspects behind the three-way electrochemical interactions. The strategy to examine the three-way electrochemical interactions of Pt(111) – graphene- electrolyte interface is to isolate the region for individual interaction and investigate them. The first part of the talk focuses on understanding electrochemical interaction between the graphene and the electrolyte (reaction over 2D crystals): A detailed electrochemical analysis of graphene oxidation kinetics and graphene oxide reduction kinetics will be presented. The second part of the talk will focus on electrochemical permeation of protons through graphene: A comprehensive analysis of temperature dependence of electrosorption of proton on to Pt(111) via graphene permeation in the aqueous electrolyte will be presented. Finally, the talk will focus on understanding the electrochemical reaction below graphene. A comprehensive electrochemical study of hydrogen evolution reaction (HER) on graphene – Pt (111) electrode in the aqueous electrolyte will be presented. These fundamental-level analyses of the three-way electrochemical interaction of 2D materials would be of crucial importance for both the scientific and commercial success of 2D material.

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Atomic Pillar Effect in Pd_xNbS_2 To Boost Basal Plane Activity for Stable Hydrogen Evolution

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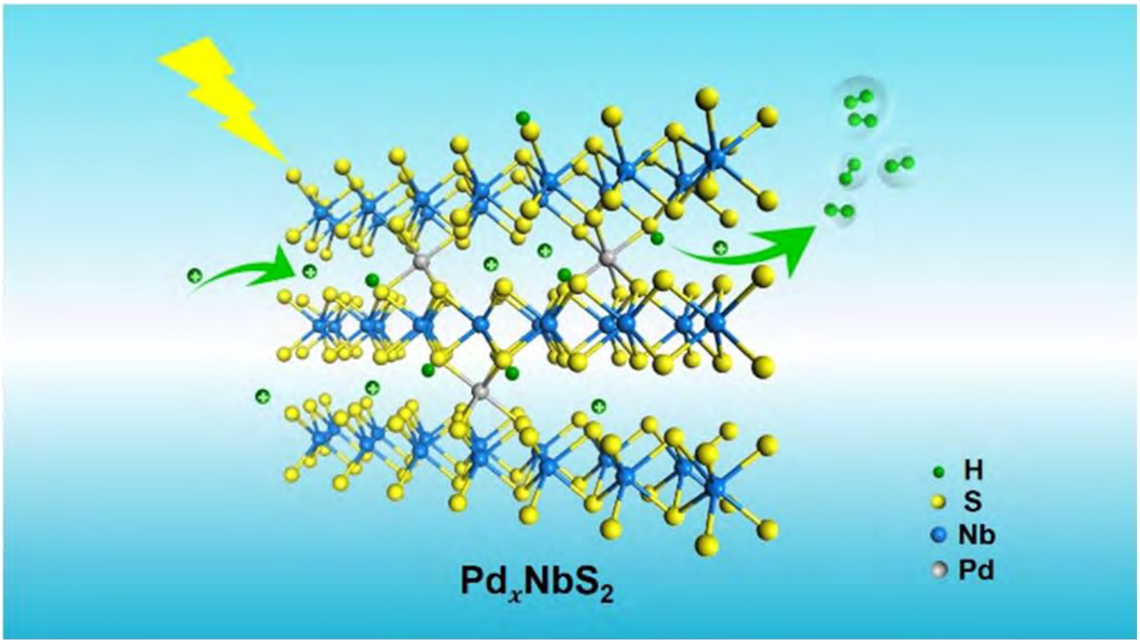
ABSTRACT: Exploring novel electrocatalysts with prominent performance is highly demanded for electrochemical hydrogen evolution. As one family member of layered transition-metal dichalcogenides (TMDs), metallic niobium disulfide (NbS_2) with intrinsic basal plane activity might be a promising candidate once its electrical and structural characteristics are optimized. Here, we develop novel electrocatalysts by incorporating palladium (Pd) atoms into the van der Waals gaps of NbS_2 to form new compounds Pd_xNbS_2 (x = 0-0.23). On the basis of single crystal structure refinement and theoretical calculations, the Pd atoms act as atomic pillars to expand the interlayer spacing of NbS_2 and boost the basal plane activity with a drop of Gibbs free energy for hydrogen adsorption to 0.06 eV on neighboring S atoms, resulting in more protons to adsorb and react. In addition, pillared Pd stabilizes the crystal structure by connecting the NbS_2 interlayers with $[PdS_6]$ octahedra. All these merits endow $Pd_{0.23}NbS_2$ with superior electrochemical activity and durability, achieving 10 mA cm^{-2} at a low overpotential of 157 mV with a negligible change in 12 h. This unique atomic pillar effect for optimizing the electrocatalytic performance of Pd_xNbS_2 demonstrates a functional and powerful strategy to develop efficient TMD-based electrocatalysts.



Guidelines for the Voltammetric Study of Electrode Reactions with Coupled Chemical Kinetics at an Arbitrary Electrode Geometry

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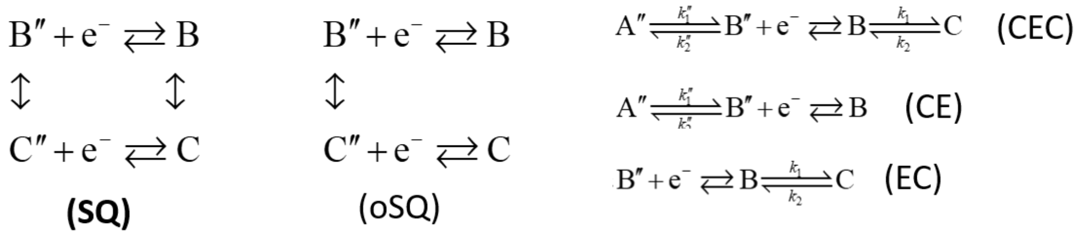
By suitable preliminary analysis of the boundary value problem, a remarkable generalization and simplification of the theoretical treatment of homogeneous chemical reactions affecting the interfacial charge transfer is revealed for any electrode size and shape [1,2]. Thus, the multivariable boundary value problem of complex reaction mechanisms [3], at both uniformly accessible (as(hemi)spheres) and non-uniformly accessible (as discs) electrodes, can be reduced to a single variable problem the mathematical form of which is equivalent to that of an irreversible E mechanism. This is obviously very advantageous for the mathematical resolution of the problem either by analytical or numerical methods.



In this communication, the use of the above theoretical approach is illustrated by treating the problem of the SQ mechanism and the simpler derived schemes oSQ, CEC, CE and EC [4,5]. The solutions obtained enable the comprehensive study of their voltammetric response as a function of the chemical rate and equilibrium constants and of the electrode size and shape. As a result, clues and experimental protocols for the identification and characterization of the charge transfer mechanism and for the determination of the corresponding kinetic and thermodynamic parameters are established. Also, the equivalence relationship between electrodes of different shape is critically examined within this context, finding that the constant relationship between the steady state current−potential response at microdiscs and micro(hemi)spheres (ratio between the current densities at electrodes of the same radius = 4/π) does not hold in the presence of chemical kinetic effects, even though the electron transfer is Nernstian.

Acknowledgements

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Spectrally Selective PANI/ITO Nanocomposite Electrodes for Dual Band Dynamic Windows

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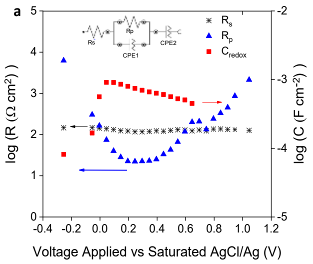
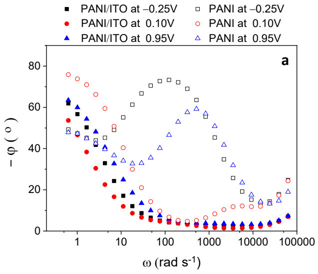
Chromogenic materials are able to change their optical properties as a response to an external stimulus, such as light irradiation (photochromic materials), temperature variation (thermochromic materials) or electric potential (electrochromic materials).

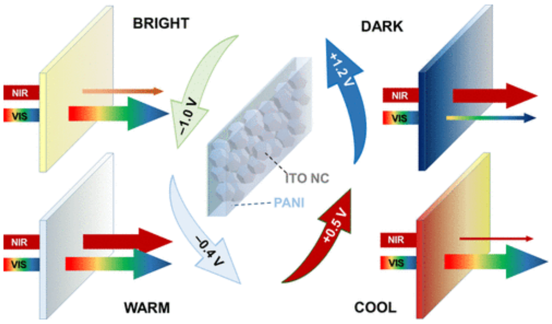
Glazing employing electrochromic materials can change their optical characteristics of transparency and absorption of solar radiation according to users' needs by simultaneously reducing visible light and NIR transmission through the window. However, spectral selectivity has been becoming a key requirement in smart dynamic windows as it permits maximizing both visual and thermal comfort while minimizing energy consumption for heating, cooling, and lighting [1].

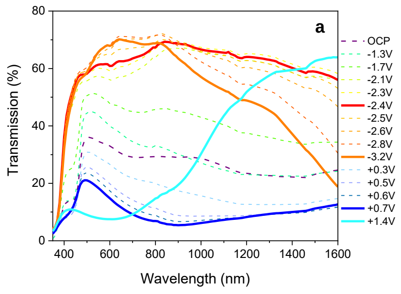
Herein, a dual band electrochromic system is presented, which consists of an engineered nanocomposite electrode capable of advantageously combining the broad band plasmonic response of nanocrystalline indium-tin-oxide (ITO) with high optical contrast of polyaniline (PANI). Their synergistical spectroelectrochemical features make possible the implementation of a four-state tunable electrochromic system (here referred to as "plasmochromic"), which permits selectively regulating optical transmittance in the visible and near-infrared range and exhibits excellent spectral selectivity across a potentials window of only 1.2 V, with a visible light *vs.* solar transmittance ratio tunable from 0.67 to 1.61.

Electrochemical and spectroscopic features of the two constituting components (*i.e.*, ITO nanocrystals and PANI) will be discussed, together with the study of how their single characteristics symbiotically combine each other in defining the performance of the resulting hybrid plasmochromic electrodes. Finally, a set of dual-band EC devices offering an excellent VIS/NIR spectral selectivity within a relatively small electrochemical window will be presented, discussing their main key features [2].









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Oxidation ratio of conducting polymer in the conducting polymer-coated electrode

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A solid electrode that can operate as both a reference electrode and a counter electrode—a reference/counter electrode—for an organic phase, Org, is necessary for the fabrication of a micro and/or thin layer cell with an organic membrane such as a liquid membrane-type ion-selective electrode, ISE, and a voltammetric cell with the interface between aqueous phase, W and Org.

A conducting polymer-coated solid electrode has been one of candidates for use as a reference/counter electrode in Org. The conducting polymer has low solubility in Org and functions as an ion-electron transducer. In 1987–1988, the conducting polymer-coated electrode was applied to an all-solid ISE in which the inner solution was replaced by the conducting polymer, and there are many reports on the all-solid ISE using the conducting polymer-coated electrode even in recent literatures. Recently, amperometric ISEs and the coulometric thin layer cell using the conducting polymer-coated electrode have been proposed and used for the realization of stripping voltammetry and absolute determination of redox-inactive ions. However, these ISEs and electrolysis cells with the conducting polymer-coated electrode have rarely been used in practical applications even though various applications of the conducting polymer-coated electrode have been proposed.

Low stability and poor reproducibility of the electrode potential are the most serious problems for the conducting polymer-coated electrode. Poly(3,4-ethylenedioxythiophene), PEDOT, is a chemically stable conducting polymer that improves the potential stability of the all-solid ISE; however, slow potential drift and a shift of the absolute value of the electrode potential in an aqueous standard solution have been observed for this ISE. The factors related to the potential stability and reproducibility of the conducting polymer-coated electrode have been extensively discussed based on the redox capacitance of the conducting polymer or the irreversibility of the ion transfer between the polymer and the selective membrane.

To get stable and reproducible potential for longer period, we adopted the potentiostatic adjustment of the oxidation ratio: the formal potential for the redox reaction of the conducting polymer was evaluated from the potential dependence of the absorption spectrum of the conducting polymer and was applied to the conducting polymer-coated electrode for adjustment of the oxidation ratio. The potentiostatic adjustment for long time made more homogeneous oxidation condition in the conducting polymer while chronocoulometric adjustment for short time made inhomogeneous oxidation condition. The potential stability and potential reproducibility of the conducting polymer-coated electrode under open circuit or current-flowing were examined in hydrophobic Orgs for longer period such as 200 h by focusing on the oxidation ratio of the conducting polymer. Oxidation to the conducting polymer by oxygen in air was also examined for 800 h. The partially oxidized PEDOT electrodes were applied to the two-electrode system thin layer cell for the ion transfer between aqueous sample solution and organic membrane [1].

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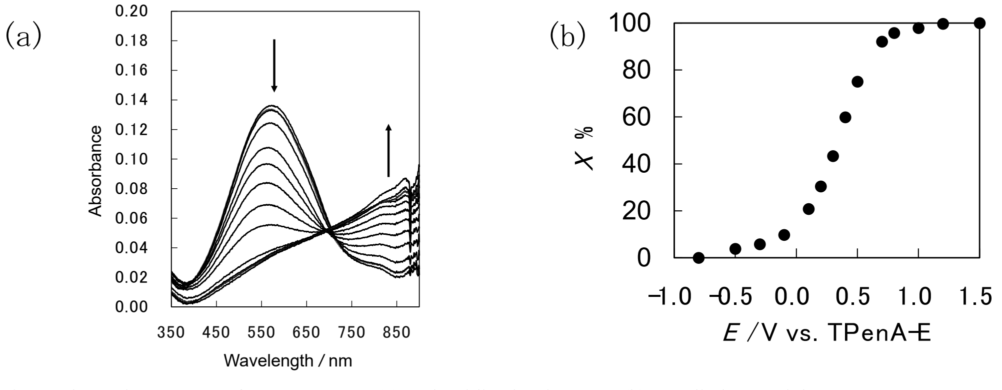
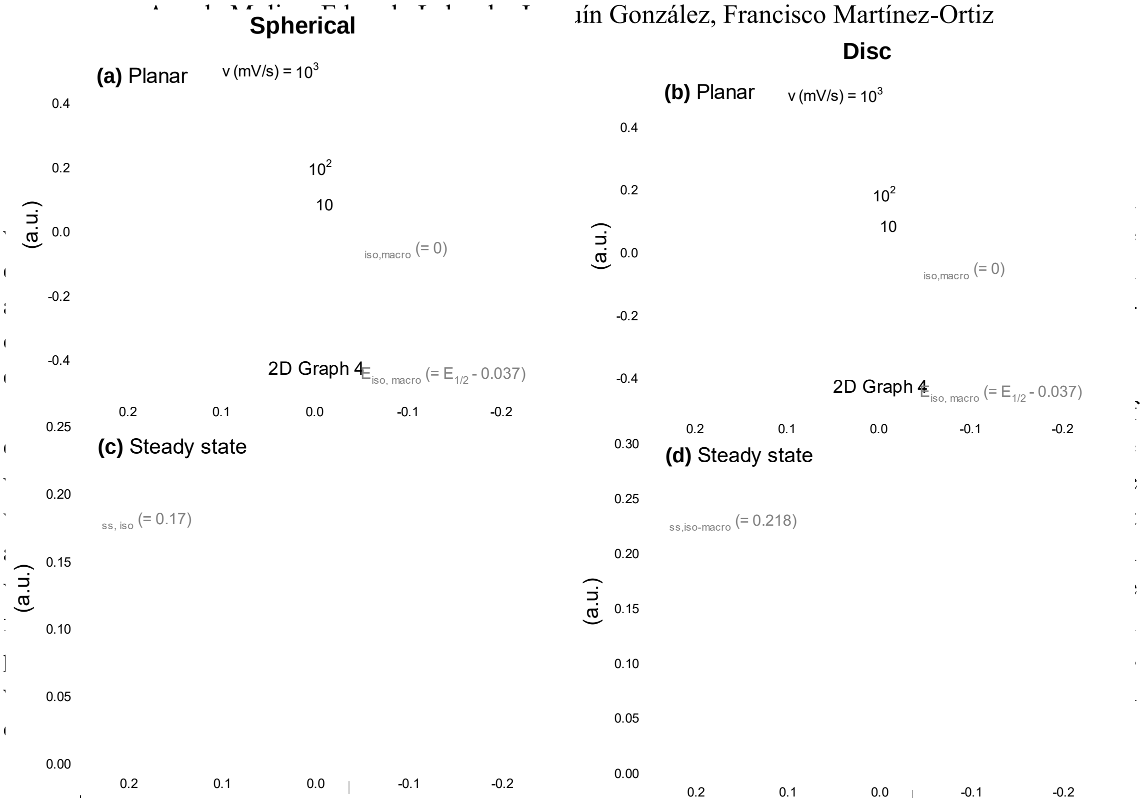


Fig. 1 Absorption spectra of PEDOT-ITOE (a) and oxidized ratio, *X* %, (b). Applied potential: -0.8, -0.5, -0.3, -0.1, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 0.8, 1.0, 1.2, 1.5 V; thickness of the PEDOT : 8 mC cm^{-2}; electrolysis period: 10 s.

Voltammetry of Reversible Electrode Reactions with Complex Stoichiometry at Electrodes and Microelectrodes

ín González, Francisco Martínez-Ortiz



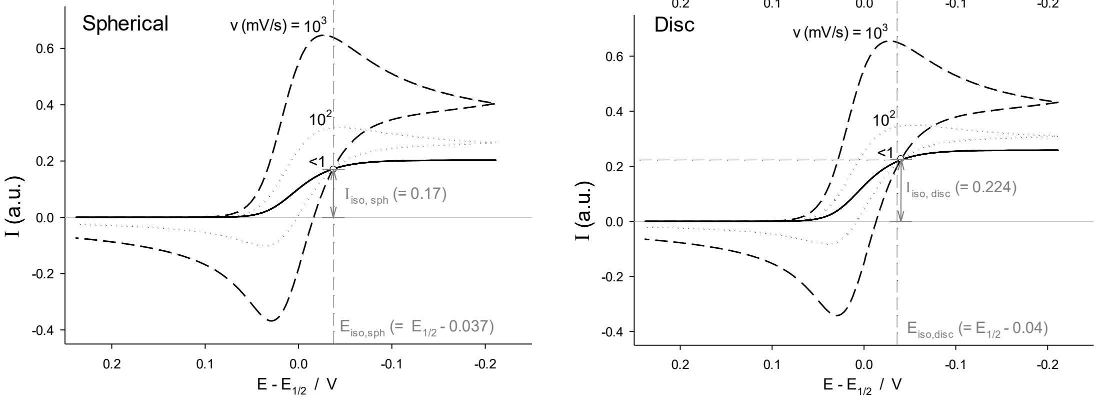


Figure 1. Cyclic voltammetry of the 2:1 stoichiometry with *n*=2 at (hemi)spherical and disc electrodes of radius r_0= 25 µm [4].

Acknowledgements

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Electrochemical detection of Prussian Blue Nanoparticles in flow

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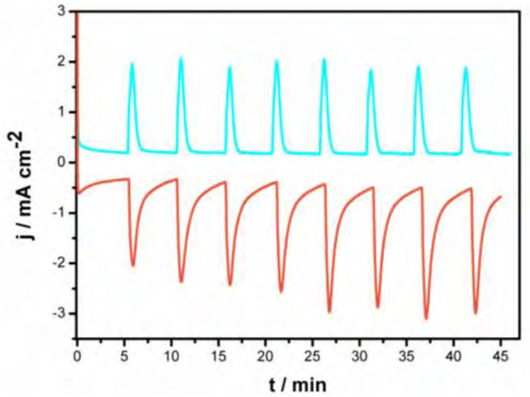
The last decade has abounded in research on the electrochemical behaviour of suspended nanoparticles. Most of them focused on their electrochemistry at an ultramicroelectrodes in quiescent conditions. Detection of single collisions of nanoparticles with the (ultra-micro)electrode surface was claimed[1,2]. This is important from the point of view of acquiring knowledge about single nanoparticles, but it requires sophisticated equipment and skilled personnel. For many purposes including analytical ones other techniques involving the larger size of electrodes can be used. This requires acceleration of nanoparticles, namely experiments in forced convection conditions. Recently we demonstrated electrochemical detection of nanoparticles exhibiting redox reaction: Prussian Blue nanoparticles at rotating disc electrode[3]. Here we would like to extend this study to flow conditions. For this purpose we prepared 3D printed system consisting channels, mixer, inlets, outlets, place to fix working disc electrode and chamber for counter and reference electrodes and (see scheme below). Such an approach allows for simple and quick design and optimization of the whole system including the position of the working electrode (perpendicular or parallel to the flow).

We will demonstrate that Prussian Blue nanoparticles can be detected employing both electrochemical reduction or electrochemical oxidation. The effect of the cell design, electrode material and flow rate will be demonstrated. These results, including the detection limit, will be compared with those obtained with a rotating disc electrode. [3]



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Raman spectroelectrochemistry of conducting polymer films on reflective electrode: role of double excitation of the solution layer

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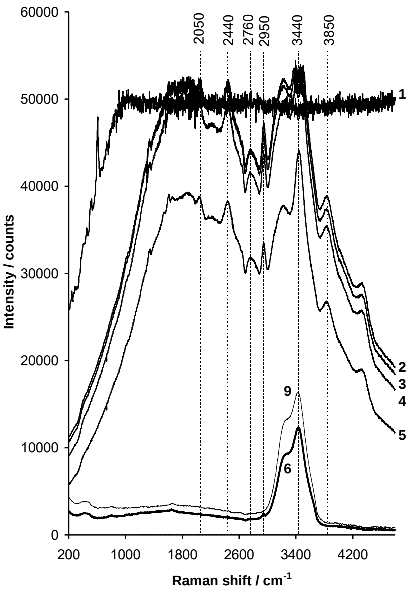
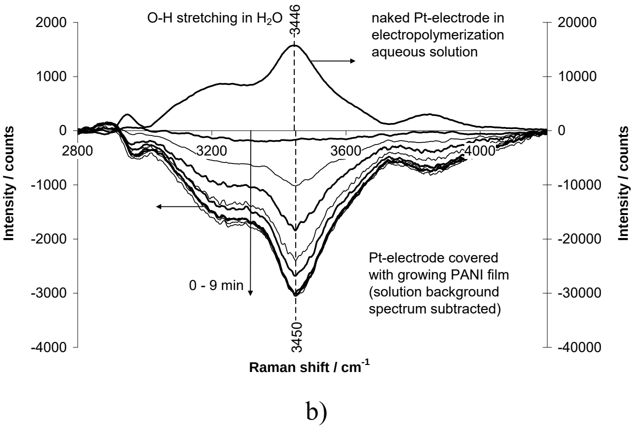
Raman spectroelectrochemistry is a powerful tool to monitor structural transformations during electrosynthesis and doping/dedoping of conducting polymers. However, the excitation laser beam passes several interfaces, where absorption, refraction and reflection processes may occur. These are: air/glass (the wall of spectroelectrochemical cell); glass/electrolyte; electrolyte/film (of conducting polymer); film/electrode. Noteworthy, the film of conducting polymer changes its thickness, absorption and refraction during the electrosynthesis and doping/dedoping. All these phenomena influence the shape of in situ Raman spectra and are also dependent on the incident angle of the laser beam. This influence was demonstrated on the example of in situ Raman monitoring of galvanostatic polymerization of aniline on Pt-electrode in aqueous solutions of the following polymeric sulfonic acids: flexible-chain poly(2-acrylamido-2-methyl-1-propanesulfonic acid), poly(styrenesulfonic acid) and rigid-chain poly-(4,4'-(2,2'-disulfoacid)-diphenylene-iso-phthalamide), poly-(4,4'-(2,2'-disulfoacid)-diphenylene-tere-phthalamide). Firstly, it was found that 532 nm laser radiation caused fluorescence in the solutions of phenyl-containing polyacids resulted in the Raman spectrometer overload. One can reduce fluorescence (Fig.a) by increasing the incident angle of the laser beam on the electrode up to 20° (perpendicular direction is taken as 0°). Secondly, some of the polyacids were found to have intensive Raman bands in the range of characteristic Raman frequencies (1000-1800 cm^{-1}) of polyaniline (PANI). In this case, subtraction of the solution background spectrum before starting the electropolymerization monitoring causes appearance of ever-growing negative Raman signals (Fig.b) as the PANI film absorbing the laser radiation grows on the reflective electrode. The above two issues are due to the double excitation of the thin solution layer before the electrode by the incident and reflected laser beams, the degree of this doubling decreasing as (1) the incident angle is increased and (2) the laser-absorbing PANI film grows. The distortive influence of the solution Raman spectrum on the real shape of PANI spectrum may be estimated and diminished by using the amplitude of ever-growing negative Raman signal in the area of water O-H vibration (near 3440 cm^{-1}) as a measure of the ever-decreasing reflectance of the working electrode. Using the developed approach, it was shown that evolutions of the relative portions of the imine nitrogen (near 1490 cm^{-1}) and the radical-cation nitrogen (near 1340 cm^{-1}) fragments in the Raman spectra of PANI recorded in the course of electropolymerization can be used as informative criteria for the explanation of the differences in the aniline polymerization rate in the presence of polyacids of different chemical structure.



a)



b)

Fig. Raman spectra: a) of Pt-electrode at different incident angles of the laser beam in the polymerization baths based on i-PASA (1 – 0° (16 mW), 2 – 10° (16 mW), 3 – 15° (16 mW), 4 – 20° (16 mW), 5 – 20° (14 mW)); PAMPSA (6 – 20° (14 mW)); Pt-electrode in water (9 – 20° (14 mW)); b) of water O-H stretching vibration in the i-PASA bath and its evolution before growing PANI film (background subtracted).

This study was supported by the Russian Foundation for Basic Research, project No. 19-29-08048_mk.

Greywater Treatment with Microbial Fuel Cells: Organic Matter Removal and Energy Production

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A fraction between 60 and 75% of domestic wastewater is represented by greywater, which can be defined as water coming from domestic sources, including kitchen sinks, washing machines, and hand basins excluding toilets, bidets, and urinals. Compared to unsegregated domestic wastewater, greywater contains a relatively lower amount of organic matter that needs to be removed in order to comply with the current regulations regarding water reuse for non-potable application.

Among different options for greywater treatment, membrane filtration and its coupling with biological treatment, membrane biological reactor, are particularly diffused due to the simplicity and compactness of the treatment. However, those technologies are highly energy consuming, and may negatively impact on the energy balance of a building.

Bioelectrochemical systems (BESs) have emerged in the last two decades as a multi-faceted platform for a variety of purposes, including organic matter removal, nutrients recovery, hazardous sites remediation, groundwater treatment. The first and most common declination of BESs is represented by microbial fuel cells (MFCs), able to remove organic matter and produce electrical energy.

In this work, 3 identical H-type MFCs were built, inoculated and then operated for the assessment of the suitability of greywater treatment for organic matter removal and energy production. Due to the large variability of conductivity in greywater, a single MFC was operated with low conductivity greywater (348 µS/cm), a second one with high conductivity greywater (1578 µS/cm); a third one was fed with acetate and used as control reactor. Each batch was repeated 3 times to ensure reproducibility. Organic matter concentration of greywater and acetate solution was measured at 489 mgCOD/L; each batch lasted 500 hours.

A similar organic matter removal was observed in the different MFCs, with values between 85% (greywater, high conductivity) and 90% (acetate fed), showing that the MFCs were able to oxidize the complex organic compounds present in greywater. As shown in table 1, the performances in terms of electrical production of the MFC fed with high-conductivity greywater were higher than in the case of low conductivity influent. In addition, the maximum voltage in the case of low conductivity greywater was reached more than 200 hours later compared to the high conductivity greywater-fed MFC.

Table 1. Organic matter removal and electrical production data from the third batch of the experimentation. NER: Normalized energy recovery; CD_{max}: maximum current density; PD_{max}: maximum power density; V_{max}: maximum voltage.

Test	NER_s (kWh/kg_{CODrem})	CD_{max} (mA/L)	PD_{max} (mW/L)	η_{COD} (%)	V_{max} (mV)
Greywater, low conductivity	0.15	0.84	0.29	87%	346
Greywater, high conductivity	0.21	0.98	0.40	85%	409
Control, acetate	0.34	1.14	0.54	90%	474

Low conductivity in wastewater usually causes increase of overpotentials, due to slow proton transport in the active biofilm, enhanced resistance in ion transport between anode and cathode, other than higher resistances originating from the diffusion boundary layer and electric double layer. The combination of these factors may have led to the observed decrease in MFC's energy production.

In conclusion, MFC technology showed to be able to successfully remove organic matter from greywater, allowing also the production of electrical energy. This findings may open a novel pathway for an on-site treatment of greywater for non-potable reuse coupled with energy recovery that may be directly used in the building in which greywater is collected and treated.

Bimetallic Organic Framework Deposited on Anodized TiO_2 Nanotube Arrays with Enhanced Photoelectrochemical Activity for Water Oxidation

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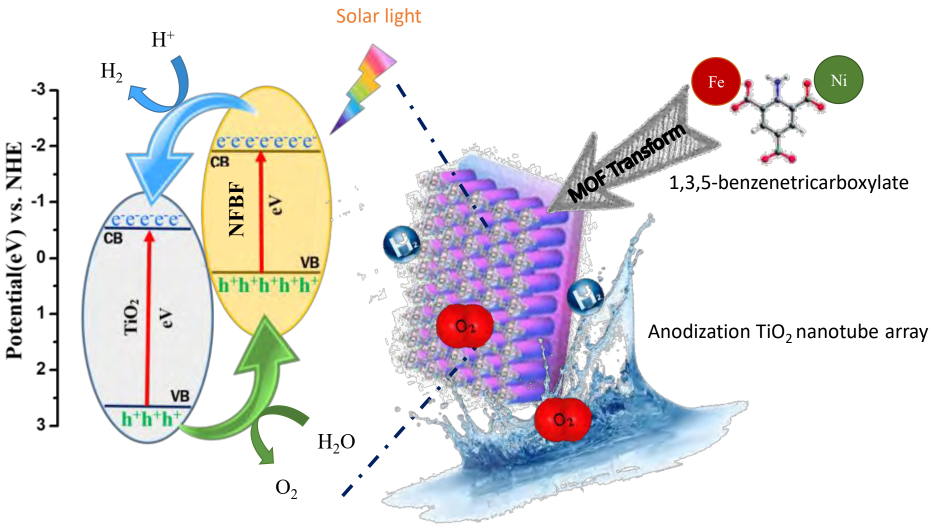
Fossil fuel reserves are dwindling and their unrestricted use has led to incontrovertible changes in the Earth's surface temperature and climate. Solar fuel generation through water splitting is an ideal route to store renewable energy sources and mitigate global warming. Metal organic frameworks (MOFs) have recently been used as solid supports in photocatalytic water splitting. Their porosity and structural versatility offer a tantalizing consolidation of the components needed for solar light harvesting and water dissociation. In this work, we report on the fabrication of iron-nickel bimetallic organic framework (FNBF) discretely deposited on top of anodized TiO_2 nanotube array (TNTA). They were synthesized by electrochemical deposition of Ni^{2+} and Fe^{3+} species onto TNTA surfaces and then chemically transformed (using a simple hydrothermal process) into MOF by using appropriate organic ligands. The structures of these photanodes was optimized and characterized by SEM, TEM, and XPS analysis. The optimized FNBF@TNTA photoanodes were then tested for water photo-oxidation. A photocurrent of 1.40 mA cm^{-2} was measured under 100 mW/cm^2 UV + Visible light intensity. The performances were found stable (a photocurrent of 1.30 mA cm^{-2} was measured after 180 minutes of continuous operation). These nanocomposite photoanodes successfully combine great light harvesting properties, a good conductivity and stability due to the carbon-based architecture, and show good oxygen evolution reaction activity under solar light. FNBF@TNTA photoanodes are promising materials for the development of water



Coupling microalgae and microbial fuel cells: process optimization for simultaneous wastewater treatment and energy recovery

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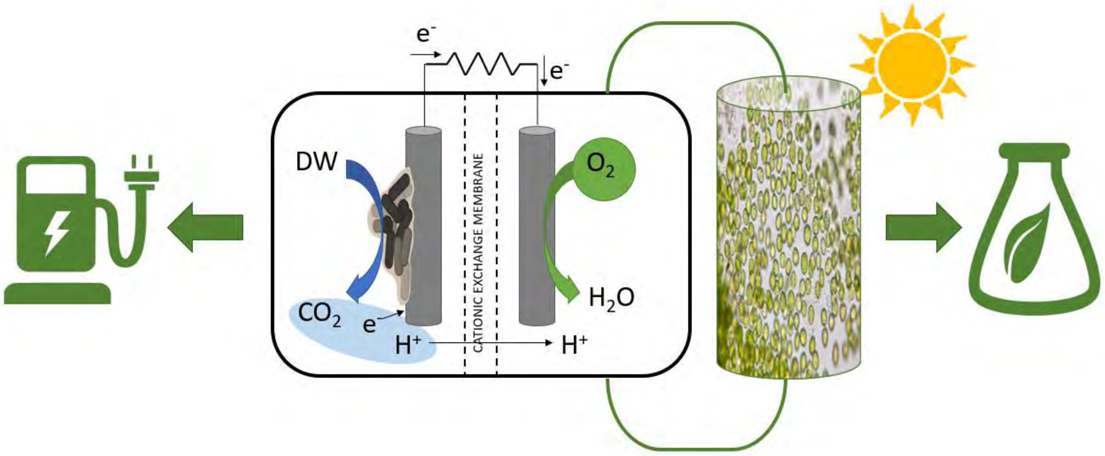
Increasing energy demands and greenhouse gases (GHG) emission from wastewater treatment processes prompted the investigation of alternatives capable to achieve effective treatment, energy and materials recovery, and reduce global environmental footprint.

Microbial fuel cells (MFCs) are a promising technology for wastewater treatment, characterized by electrical energy recovery and low emissions and sludge production. MFCs convert the chemical energy of organic pollutants (substrate) directly into electrical energy, thanks to electrochemically active bacteria (EAB) in the anodic chamber, potentially achieving higher conversion efficiency (44%) than with a conventional anaerobic treatment (28%). Microalgae, on the other hand, are well known as potential candidates in biorefineries for biofuels and biomaterial production, because of the many products that they can potentially produce with lower land occupation and no competition for human nutrition needs.

Coupling MFC technology with microalgal-based process in MFC-PBR (photobioreactor) systems could reduce GHG emissions from wastewater treatment facilities, capturing CO_2 emitted from industrial facilities or directly from the atmosphere and convert it in the desired terminal electron acceptor (TEA), oxygen. Microalgae production could enhance recovery of wastewater-embedded resources. Two identical MFC-PBR systems configurations were tested and compared with a control MFC, under different operating conditions (light/dark ratio, oxygen providing method), using both synthetic and agro-industrial wastewater as anolytes. COD removal efficiency (ηCOD) and energy production were monitored throughout the experimentation, reaching ηCOD values up to 99% and power density (P_d) up to 2.8 W m^{-3}. Energy losses were also evaluated to monitor how the presence of the microalgae affected the long-term operation of the system. The system equipped with microalgal biocathode proved to be capable to efficiently treat real wastewater, achieving values comparable to the control system. Oxygen provided by the algae improved the overall energy balance of this system by lowering aeration costs, which could be further enhanced by post-processing of the cathodic microalgal effluent.



Oxygen Supply Management to Intensify Domestic Wastewater Treatment by a Microbial Electrochemical Snorkel (MES)

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Keywords: Electroactive biofilm, microbial electrochemical system, bioremediation process, microbial fuel cell

Oxygen supply is the most cost-intensive part of the aerobic biological wastewater treatment plants. The Microbial Electrochemical Snorkel (MES) is a low-cost and low-maintenance solution that should considerably reduce this cost. A MES is generally in the form of a single electrode placed vertically in an environment where the composition of oxidizing and reducing species is spatially heterogeneous.

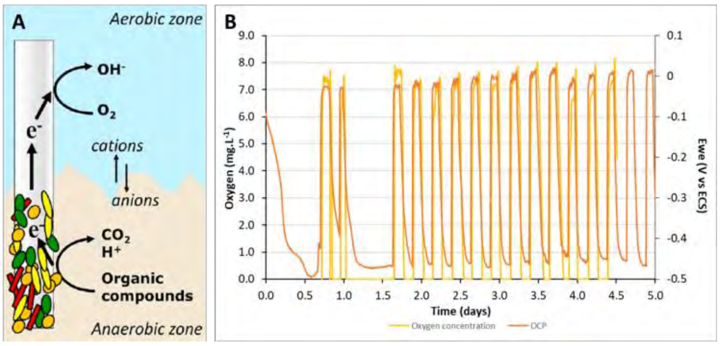

Figure 1 : (A) Principle of the Microbial Electrochemical Snorkel (B) Evolution of the dissolve oxygen concentration and the OCP

In the context of wastewater treatment, the lower part of the MES (Figure 1-A), is positioned in the anaerobic environment and ensures the oxidation of the COD (Chemical Oxygen Demand) present in the effluent to be treated [1,2]. Anaerobic bacteria spontaneously form an electroactive biofilm on the surface of that part of the MES and oxidizes the COD by transferring electrons to the electrode. This part of the MES acts as the electron acceptor (microbial anode). The upper part of the MES, located in the aerobic zone, ensures the evacuation of the electrons via the oxygen reduction reaction (cathode). The objective of the work was to optimize the oxygen supply in the upper aeration zone.

The challenge was to solubilize the amount of oxygen required for the extraction of electrons without disturbing the lower anaerobic zone. We have demonstrated that the efficiency of the COD abatement by MES depends on the open circuit potential (OCP) of the MES. Furthermore, the OCP and the soluble oxygen concentration are closely related (Figure 1-B). This correlation was used to optimize the operating protocol of the MES. Several types of reactors have been set up by varying the height of the aeration zone, the aeration mode, continuous or sequential, and its frequency.

The liquid phase of the reactors was aerated by air bubbling, which provides intensive gas-liquid transfer to ensure 100 % of O_2 solubility in the upper cathodic part of the MES. In response to aeration, the OCP of the MES increased by promoting the cathodic reaction until a high potential was reached around 0 V vs. SCE (Figure 1-B). When the OCP of the MES was high, oxygen availability was no longer rate-limiting and aeration was consequently stopped. The OCP then dropped after aeration had been stopped if the anode part of the MES is fully active and ensured efficient oxidation of the COD. Oxygen availability becomes rate-limiting again when the OCP of the MES is less than -0.4 V vs. SCE (Figure 1-B). This value was reached in around 30 minutes in our systems. When the OCP was lower than -0.4 V vs. SCE, there was no further COD treatment. In control reactors, COD abatement ceases as soon as aeration was stopped. The MES therefore made it possible to abate COD, even after aeration has been stopped, contrary to the control.

The aeration frequency was then optimized taking into account that too high aeration frequency can lead to aerobic oxidation of the COD (biological respiration), which is a nuisance to the desired bioelectrochemical oxidation. Finally, a sequential aeration with 30 minutes of aeration on top of the tank for 1h30 without aeration seemed to be the most appropriate.

The work is carried out within the framework of the ANR Biotuba project (ANR-17-CE06-0015-02).

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New spectroscopic tools for single-molecule junctions

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Biological charge transport (CT) is the key step in many basic cellular processes, such as respiration or photosynthesis, and nature has developed highly specialized molecular building blocks to achieve it with unprecedented efficiency. Understanding the mechanisms behind biological CT, is key to elucidate the changes in its regimes caused by specific structural variations of the associated molecular machinery. Such knowledge will ultimately lead us to tailor its electrical properties and exploit them, in the near future, as high performance bioelectronic devices with a wide variety of applications in organic electronics, sensing, biomanufacturing etc.

To investigate CT in single-molecule bioelectronic devices, we exploit Scanning Tunnelling Microscopy-based approaches in the break-junction mode (STM-BJ)[1,2] under electrochemical control (EC-STM). It allows the trapping of individual molecules in a junction to characterize their main electrical signatures (*Fig. 1*).[2,3] We carry on our tunnelling transport studies in bio-inspired wires employing Azurin molecules (blue copper proteins) under electrochemical control. Azurin molecules present a classical metal-mediated *two-step tunnelling* transport, that results in a molecular conductance maximum when the electrochemical gate potential is adjusted to its characteristic redox midpoint value.[4] Such distinctive electronic behaviour allows to study deviations of the electron transport mechanism through the molecule, making Azurin a suitable test-bench for singe-molecule transport measurements.

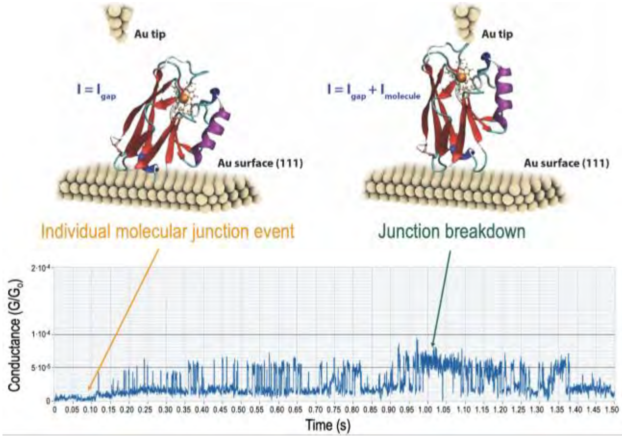

Figure 1. *Schematic representation of a metalloprotein molecule (Azurin) contacted between the STM electrodes and the captured current signal with single-molecule events which define the characteristic telegraphic-like stochastic switching.*

We will base this contribution by showing the work in progress on the development of a new hybrid platform with spectro-electrical single-molecule detection capabilities under ambient conditions. It aims to explore several key structural and physicochemical aspects, that remain unknown, during the single-molecule junction formation. This is possible thanks to the *operando* capabilities of the hybrid platform to work in the near-field Raman between the two STM electrodes (TERS) under electrochemical control. TERS represents a high ultra-sensitive non-destructive spectroscopic method with molecular resolution (*Fig. 2*). This new platform opens the gates to obtain detailed insights into the molecule's physical and chemical properties by simultaneously capturing the current during the spontaneous formation of a molecular junction, *i.e.* the evolution of spectro-electrochemical characteristics of the junction. In addition, due to the development of the new platform, novel singe-molecule effects under red-laser illumination (633 nm) have been revealed. Effects over the molecular conductance and transport mechanisms consequence to expose individual molecular junctions to a plasmonic field.

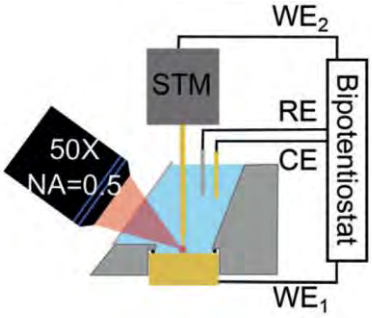

Figure 2. *TERS cell and 4-electrode configuration for electrochemistry.* [5]

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Catalysis of Redox-Neutral Reactions by Electron Exchange Between Electrodes and Organic Compounds

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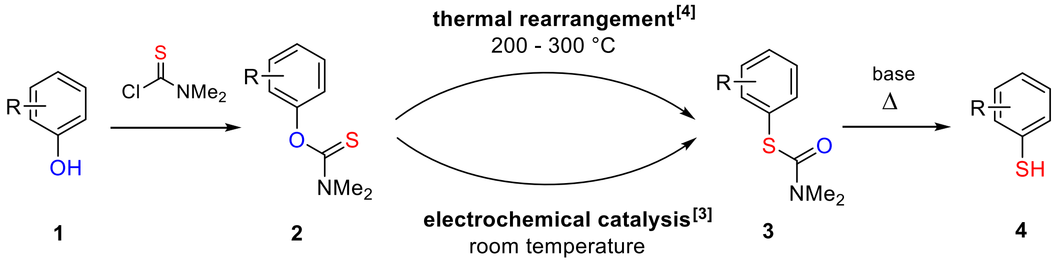
To most chemists the term ‘electrocatalysis’ is known as the facilitation of a heterogeneous electron transfer via a chemical interaction between the electrode and a substrate.[1,2] The opposite case, the utilization of a heterogeneous electron exchange to catalyze a chemical reaction (‘electrochemical catalysis’), is a much less known but yet a very powerful approach in electrosynthesis.[3] Here, the injection (or removal) of an electron into (or from) a substrate triggers a redox-neutral reaction (e. g. a molecular rearrangement) that may otherwise require harsh conditions and/or the use of reagents. Such processes involve the electrogeneration of an ionic or radical ionic species, which after a coupled chemical step either undergoes a backward electron exchange with the electrode (ECE^{b} mechanism) or triggers a chain process in the bulk solution. Under these circumstances, sub-stoichiometric amounts of charge are sufficient to achieve a full conversion and conceptionally, the electrons and holes can be understood as being catalysts.

In this contribution, the concept of electrochemical catalysis will be illustrated using the Newman-Kwart rearrangement (NKR) of *O*-aryl thiocarbamates **2** to the corresponding *S*-aryl compounds **3** as an example (see scheme below).[4] Generally, the NKR represents the key-reaction in the three-step synthesis of thiophenols **4** from phenols **1** and proceeds between 200 and 300 °C.[5] Electrochemical catalysis, however, allows for operation at room temperature and provides a complementary reactivity with respect to the arene substitution.[4] Recently, we have carried out a detailed mechanistic study using cyclic voltammetry, control experiments and quantum chemical calculations,[6] the results of which will be presented herein.



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Electrochemical Properties of Ru and Os Organometallic Complexes: Effect of Adsorption

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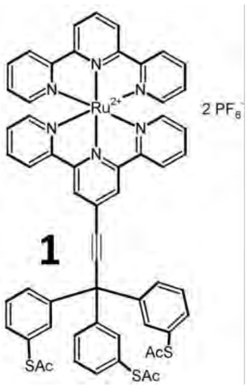
Organometallic complexes based on M(terpyridine)$_2^{2+}$ offer wide range of use for their photophysical and photochemical properties.[1,2] These molecules rank among the promising group of compounds for molecular electronics, new electrochromic devices and sensors. The aim of this contribution is a preparation and characterization of compact films of M(terpyridine)$_2^{2+}$ (M = Ru, Os) organometallic complexes on the electrode surface. Electrochemical behaviour of adsorbed molecules will be compared to their electrochemical properties in solution. One of the possibilities of molecular film preparation is structural addition of linker terminated by functional groups specialized for the formation of Au-S bond between molecule and gold electrode.[3] Tripodal arrangement of anchoring groups supports formation of fully compact self-assembled monolayers (SAMs) of redox active centers perpendicular to the electrode surface.[4]



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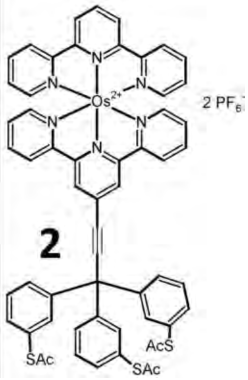

2

The electrochemical properties of organometallic complexes **1** and **2** (for chemical structure see attached figure) were studied by cyclic voltammetry at various scan rate values in acetonitrile in non-adsorbed state on gold and glassy carbon electrodes and in the form of SAMs on the polycrystalline gold electrode. Cyclic voltammograms of **1** in non-adsorbed state show reversible voltammetric wave for Ru^{2+}/Ru^{3+} oxidation at E^0 = +0.910 V vs. Fc/Fc$^+$. Value of E^0 obtained for Os^{2+}/Os^{3+} oxidation of **2** was +0.562 V vs. Fc/Fc$^+$. These values are similar to E^0 values obtained for metal ion oxidation of the reference Ru(terpyridine)$_2^{2+}$ and Os(terpyridine)$_2^{2+}$ complexes.[2,5] Diffusion-controlled process was proved by a linear dependence of the oxidation peak current on the square root of the scan rate. Terpyridine ligands of **1** and **2** are reduced in two one-electron reversible processes and their E^0 values are shifted positively in comparison to M(terpyridine)$_2^{2+}$ complexes indicating easier reduction of newly prepared molecules **1** and **2**. SAMs of **1** and **2** were prepared by standard procedure.[4] Ru^{2+}/Ru^{3+} oxidation of **1** was observed at E^0 = +0.948 V vs. Fc/Fc$^+$, that of Os^{2+}/Os^{3+} oxidation of **2** was measured at +0.587 V vs. Fc/Fc$^+$. Adsorption of **1** and **2** was proved by linear dependence of peak current on the scan rate. The determined values of the surface concentration of **1** and **2** indicate that the molecules form compact monolayer, where all of the Au-S bonds are involved in the SAMs formation. SAMs of **2** are more compact compared to SAMs of **1** due to different management of Coulombic interactions within the SAMs.

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Unveiling the electronic properties of lithium ion materials trough electrolyte gate transistor set-up

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Lithium ion batteries have been and are one of the major components in the portable electronics revolution, as well as in the transition to a more sustainable society based on electric mobility. To advance in this field, the research is strongly committed in the development of new nanostructured electrode materials, and in the deep understanding of the processes that are involved during charge/discharge.

Electronic and ionic transport at the electrolyte/electrode interface play a critical role during battery operation. In situ and in operando techniques represent powerful tools to investigate such phenomena. Electrochemical Impedance Spectroscopy (EIS) has been widely exploited to study the response of the electrode at different state of charge. This technique demonstrated that electrode impedance evolves during lithium intercalation mainly because of the formation of the solid electrolyte interphase. However, in the case of metal oxides EIS has also indicated that the inherent electronic properties of electrodes changes with the degree of lithiation. Despite excellent models have been proposed, EIS still does not enable a clear discrimination between the effect on the impedance of the charge transfer at the interphase and the electronic conductivity of the electrodes.

To address this challenging issue, here we report for the first time a systematic study on the electronic properties of electrode materials for lithium ion batteries at different state of charge by an electrolyte gated transistor set-up. This novel configuration allows to evaluate the evolution of the electronic characteristics of the materials in situ, i.e. during the lithium ion intercalation/de-intercalation. Specifically, a study carried out on Lithium Titanate and olivine and spinel cathodes is here reported and discussed.

Acknowledgments

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Electrochemical-driven Carbocatalysis as Highly Efficient Advanced Oxidation Processes for Simultaneous Removal of Humic Acid and Cr(VI)

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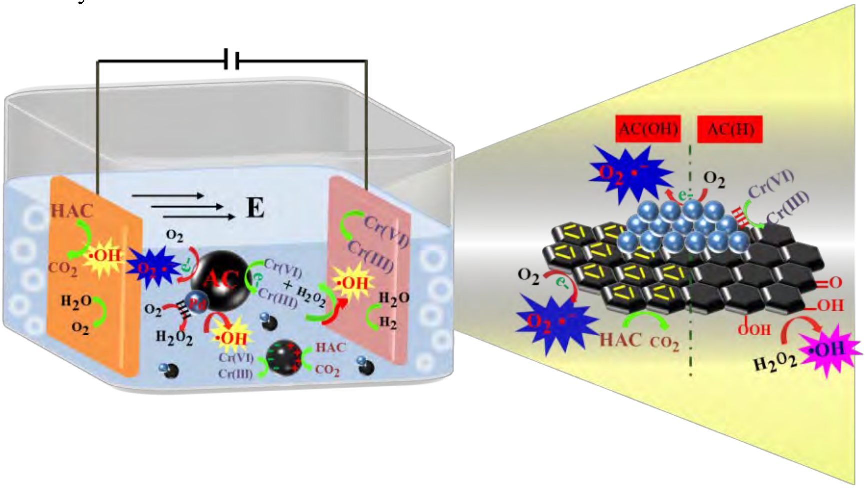
Abstract: Electrochemical advanced oxidation processes (AOPs) represent an efficient and promising strategy for dealing with the ever-growing water pollution. Meanwhile, carbocatalysis has long and widely been applied in the fields of synthesis and catalysis because of high activity and selectivity. In this work, we combined the advantages of these two methods and for the first time proposed a conceptual new, novel and promising approach of electrochemical-driven carbocatalysis as highly efficient AOPs for water remediation, which was simply performed by adding carbon-based particles into the electrochemical system. This method shows great potentials for the simultaneous removal of both humic acid (HAC) and Cr(VI) in water, in which HAC was effectively mineralized with a TOC removal efficiency as high as 90% and Cr(VI) was completely removed with a total Cr removal beyond 90%. The presence of carbon particulate materials and their physicochemical properties were first indicated to play critical roles in the developed electrochemical AOPs. These added carbonaceous particles such as activated carbon (AC) and a series of modified AC materials, on one side exerted an important carbocatalytic function with typical AOPs features and on another side, they behaved like numerous galvanic cells with quasi-homogeneous catalytic properties, greatly facilitating mass and electron transfers in the electrochemical system and resulting in a synergistic effect for the removal of combined pollutants. The physicochemical properties of these carbon particulate catalysts facilitated the simultaneous occurrence of adsorption and carbocatalysis, where a synergistic effect between adsorption and catalytic oxidation was confirmed in this electrochemical-driven carbocatalysis system. Moreover, the catalytic performances and mechanisms of this system were found to be dependent on the carbon structures (e.g., surface area, functional groups and hybridization structure, etc.). Very importantly, the energy-effective feature and the carbon materials stability showed a promising prospect of this approach with energy consumption much lower than the ever-reported electrochemical AOPs. This work details the first insight into electrochemical-driven carbocatalysis and provides a new, green and promising approach for effective water remediation, as well as gives new evidence for the synergistic effect between adsorption and catalytic oxidation.



Schematic mechanisms of carbonaceous particles-promoted electrochemical AOPs for simultaneous removal of HAC and Cr (VI).

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Carbon Paste Electrodes as Unique Membrane-Based Electrodes with Unique Performances

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Carbon paste electrodes are composed of at least carbon materials and pasting liquids. Frequently some additives are added to make modified carbon paste electrodes. Commonly, carbon paste electrodes are well known as bulk electrodes. However, electrochemical reactions occur in the surface of carbon paste electrodes. Therefore, carbon paste electrodes can be regarded as unique renewable membrane-based electrodes. The presence of both solid materials (carbon materials etc) and liquid materials (pasting liquids) in carbon paste electrodes endows them many unique features in comparison with pure solid electrodes.

We present here the application of carbon paste electrodes to enhance the stability of electrochemical generated intermediates and the electrochemical oxidation activity of azide as well as to expand electrochemical window and improve reproducibility for stripping analysis by pasting liquids (1-3).

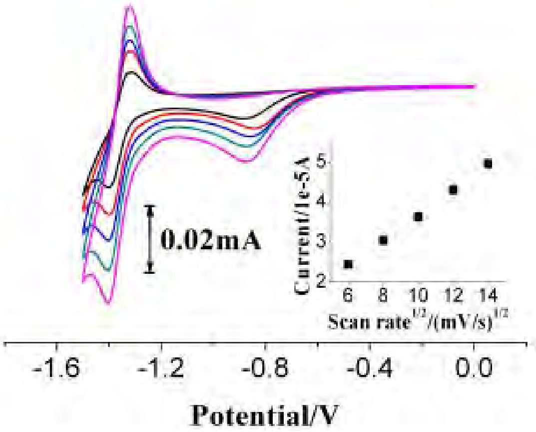

Fig. 1. Cyclic voltammogram of $Ru(bpy)_3^{2+}$ at the tricresyl phosphate-based CPE at different scan rate on in 0.1 M pH 7.5 phosphate buffer solution.

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Optimized bioreactor for coupling efficiently H_2 oxidation to NADH regeneration

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There is a growing interest for the regeneration of the cofactor NAD(P)H due to its large-scale biosynthetic applications and its high price. Different methods including: chemical, electrochemical, photochemical, microbial, and enzymatic reactions have been developed for this aim. Among all the cited cofactor's regeneration methods, the electrochemical regeneration is a continuous electron-transfer process, where the regeneration of NAD(P)H is loaded only with an electrode. In this work, we focus on coupling efficiently hydrogen oxidation to NAD^+ reduction. To reach this objective, we combined the electrochemical regeneration of NADH mediated by a dissolved rhodium complex on the carbon felt electrode of the cathodic compartment[1], the application of continuous flow reaction, and the hydrogen oxidation using a GDE at the anodic compartment in a single system. The Nafion membrane between the anodic and the cathodic compartments allows transfer of H^+ from the anodic to the cathodic compartment. To optimize the proposed process, various factors have been varied e.g. rhodium complex concentration, NAD^+ concentration, pH, the activation procedure for the carbon-based electrode, as well as the cell operating conditions such as the hydrogen and the solution flow rates.

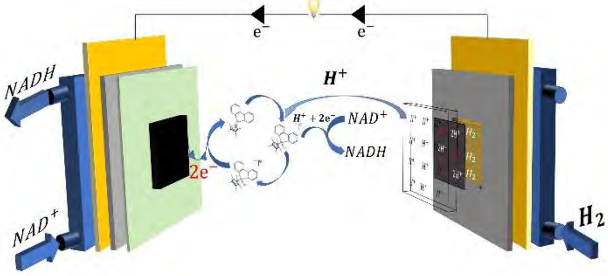

Figure 1. Functional scheme of the flow bioreactor

The efficient regeneration of NADH featured with a complete conversion and with a high faradaic yield can be reached by fixing different parameters for the used reactor: hydrogen and solution flow rates (20 mL/min), Ratio $[NAD^+]$ over $[Cp^*Rh(bpy)Cl]^+$ at 40, pH near 7 to avoid NADH and NAD^+ degradation), and with a carbon felt electrode activated in solution instead of a carbon felt thermally activated.[1]
Based on this optimized process, our actual work focuses on the covalent immobilization of the rhodium complex, that is economically desired on the laboratory and industrial scales, on the surface of a carbon felt electrode was achieved by following a two steps protocol described by us recently using a bucky paper electrode.[2,3] In addition, the rhodium complex covalent immobilization allows us to involve two reactions in the cathodic compartment: the regeneration of NADH simultaneously followed by an enzymatic reaction such as the bioconversion of D-sorbitol into D-fructose while immobilizing D-sorbitol dehydrogenase on another carbon felt. In addition, the bioconversion of D-sorbitol proves that the regenerated NADH is active and allows us to apply the regenerated cofactor as an electron carrier in enzymatic systems catalyzing stereo- and regioselective reactions having a great biotechnological potential.

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Electrochemical void pinning and liquid metal effect on electromigration resistance in 2D aluminium and copper alloys

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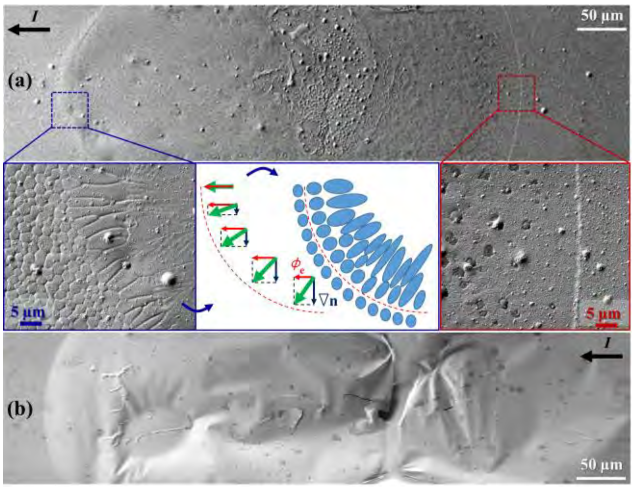
Bidimensional (2D) conducting materials in form of thin and ultra-thin films are extensively used in our daily life. The proper functioning of every solid-state or electrochemical device relies on electrical current flowing through the working electrode. In extreme situations the current density passing through a 2D wire may lead to an irreversible morphological change resulting in an open circuit condition and total device failure. This occurs due to the effect of high electron fluxes on atoms residing in the conducting material that are forced to migrate along the wire in the current flow direction. Such electromigration phenomenon is present with different intensities in any electrical device and is enhanced in 2D electrodes due to the small cross-sections through which even low voltages may induce substantial current densities. The nowadays recognized model describing electromigration is based on the concept of voids and hillocks formation. During high electron fluxes atoms will migrate pilling up material close to anode while at the cathodic side voids with increasing size will form. Thus, one way of retarding or even blocking electromigration may be thought in decreasing the surface void mobility.



The current work addresses this issue. Various thin film combinatorial libraries based on Al and Cu were tested for this purpose. Two different approaches were involved. Firstly, anodic passivation of Al and Cu alloys was applied in an attempt to remove the free metallic surface available to voids and thus pin them down making the material migration more difficult. Additionally, amorphization of Al and Cu alloys was tested by alloying them with larger atoms such as Sm. The main advantage of an amorphous 2D conducting wire would be found in a complete lack of surface grain structuring impeding the void migration. Secondly, Al and Cu 2D test wires were alloyed with Ga in a combinatorial fashion and high throughput experimentation was performed for assessing the influence of the liquid metal atoms on the electromigration process. The dynamics of such electron flux induced atomic movement was modeled and the grain boundaries pinning by Ga was demonstrated. This is briefly illustrated in the figure for one Al-Ga alloy deposited on SiO_2 substrate (a) or polymer substrate (b) for flexible electronics applications. The direction of the current flow and hence anodic and cathodic regions of the 2D test wire are visible in the figure together with the central irreversibly damaged zone. In conclusion, several routes for improving electromigration resistance of Al and Cu 2D alloys were tested. Even though an electrochemical surface treatment did not prove a clear void pinning effect, still it remains an avoidable approach for improved devices. Additionally, the use of small Ga amounts alloyed with Al or Cu resulted in a clear enhancement of resistance against electromigration even in flexible electrodes deposited of polymeric substrates.

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Microcrystalline Natural Graphite–Polystyrene Composite Film – Ten Years of Its Application in the Development of Electrochemical (Bio)Sensors

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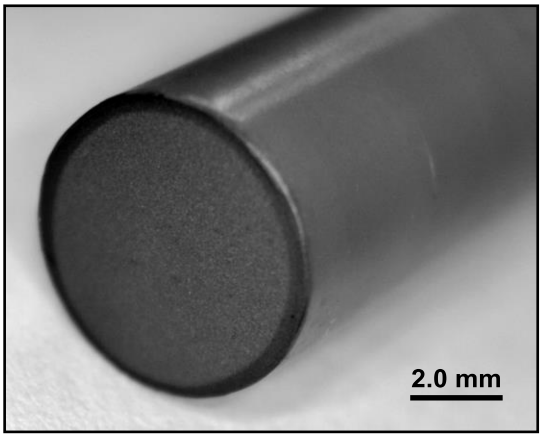
A microcrystalline natural graphite–polystyrene composite film electrode (CFE, see the Figure) [1] represents a very promising alternative to electrode surfaces modified by carbon nanoparticles with profitable electrocatalytic properties (e.g., nanotubes or graphene) as well as to commercially available disposable screen-printed carbon working electrodes. Its simple, fast, and inexpensive preparation (surface of a classical solid working electrode in a glass or plastic electrode body is covered with a carbon ink suspension – a mixture of 0.09 g of micronized natural graphite with a particle size of 3.5–5.5 μm and 0.01 g of polystyrene in 0.5 mL of 1,2-dichloroethane), simple mechanical renewal of the electrode surface (by wiping off the old film with a filter paper and forming a new one), good reproducibility of measurements, elimination of problems connected with the "electrode history", and simple chemical modification are among the main advantages [2]. Recently, it has also been shown that the CFE is a suitable transducer for the preparation of electrochemical DNA biosensors [3].



In this contribution, a complex electrochemical and microscopic characterization of the composite film will be presented, and possibilities, advantages, and limitations of this beneficial electrode material will be demonstrated on a number of electroanalytical methods utilizing the CFE-based (bio)sensors for the determination of various biologically active organic compounds (drugs [2], agrochemicals [4], environmental pollutants [5,6]) and for the detection of DNA damage induced by mutual interactions between DNA and various xenobiotic agents (chemical carcinogens [3], hydroxyl radicals [7]).

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Impact of Cr on physical and electrochemical properties of $Li_2Mn_{1-x}Cr_xSiO_4/C$ cathode material for lithium ion batteries

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Abstract: Lithium ion battery (LIB) attracted massive attention because of its high energy density, light weight, and good capacity retention like characteristics. Li_2MSiO_4 (M = Fe, Mn, V, Cr, Co, Ni, etc.) attracted attention recently due to their high theoretical energy density ~ 333m Ahg^{-1}. However, these materials suffer with strong electrochemical capacity fading because of intrinsic Jahn-Teller distortion [1] in the active cathode material together with insulating characteristics. We synthesized phase pure Li_2MnSiO_4 material and doped chromium at Mn site to circumvent some of the issues with present cathode material. The Cr^{3+} doped $Li_2Mn_{1-x}Cr_xSiO_4/C$ (x = 0, .01, .03, .06) nanocomposites are synthesized using sol-gel method. A coating of graphitic carbon on nanostructured cathode material i.e. $Li_2Mn_{1-x}Cr_xSiO_4/C$ is achieved by using carbon precursor during synthesis, Fig 1. The carbon coating is used to increase the electric conductivity and reduce the particle size by restricting the growth after carbon covering. The detailed structural and microstructural characterizations are carried out using X-ray diffraction and scanning electron microscopic measurements. Thermogravimetric (TGA) measurements are carried out to understand the amount of carbon loading and thermal degradation of cathode materials. The cyclic voltammetry and AC impedance measurements are carried out to understand the electrochemical properties and ionic conductivity of synthesized materials. XRD measurements, Fig 1, showed orthorhombic crystal structure with $Pmn2_1$ phase space group. The crystalline size for pure Li_2MnSiO_4/C samples is the largest and decreases with increasing Cr doping at Mn sites for x=0.01 and 0.06 concentration. The carbon coating is substantiating by the observed C=O vibration modes in FTIR, which disappeared in the sample after TGA measurements (up to 900 ºC). The Cr^{3+} doping in $Li_2Mn_{1-x}Cr_xSiO_4/C$ is substantiated by the observed shifting in XRD, and FTIR peaks. The oxidized carbon reduces with increasing Cr^{3+} doping, as observed in FTIR [2]. The work will discuss the impact of Cr^{3+} in terms of structural stability, and electrochemical properties such as ionic conductivity and impedance characteristics.

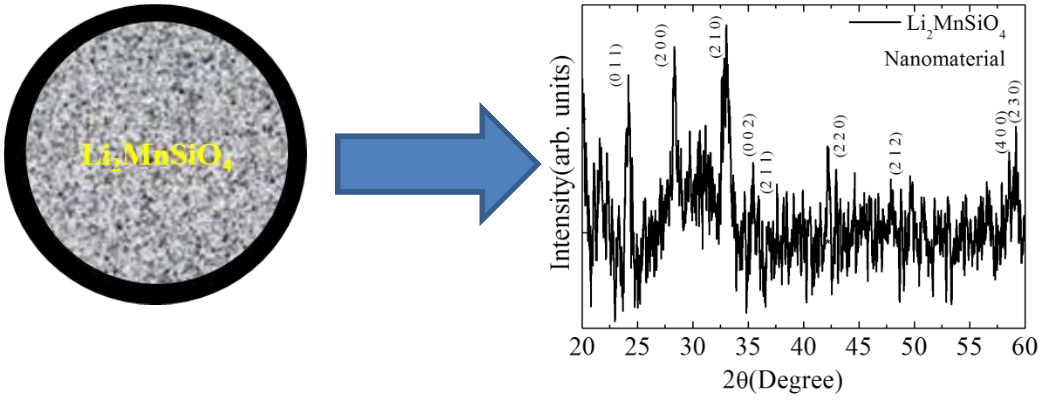

Figure 1. Schematic representation of carbon coating on cathode nanoparticles with characteristic XRD for Li_2MnSiO_4/C sample.

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Nanomaterial Modified Electrodes for Electrochemical Hydrogen Detection in Ionic Liquids

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Hydrogen is a promising "clean" fuel that produces only water when consumed in a fuel cell. However, it is explosive in nature (in air at concentrations of 4–75% by volume), which makes it a dangerous gas to store and transport. The detection of leaks of hydrogen is of utmost importance to ensure safety in future applications. Among other techniques that can be used for hydrogen detection, amperometric sensors are one type of technology that can be used for this purpose.[1] Room temperature ionic liquid (RTIL) solvents are gaining interest as replacement solvents in amperometric gas sensors as a result of their low-volatility, combined with other useful properties such as high chemical and thermal stability, wide electrochemical windows and good solvation properties. However, a challenge with RTIL solvents is the higher viscosity compared to conventional solvents can slow down diffusion and response times.

In the first part of my talk, I will discuss our work on a new design of modified electrode that can detect hydrogen very quickly upon introduction of the gas. The sensor consists of an array of gold microchannel electrodes, electrodeposited with platinum nanoparticles (PtNPs) to enable hydrogen electroactivity. Very thin layers (~9 μm) of room temperature ionic liquids (RTILs) resulted in an extremely fast response time of only 2s, significantly faster than the conventional electrodes studied.

In the second part of my talk, I will describe the modification of electrode surfaces with a metal-organic framework (MOF) as a low-cost alternative electrode material for hydrogen detection. A common MOF, HKUST-1, with copper nodes and 1,3,5-benzenetricarboxylic acid struts between them, was electrodeposited from aqueous solvents onto a glassy carbon (GC) electrode (see Figure 1). The MOF-modified GC electrode exhibited significantly enhanced activity towards the detection of hydrogen gas in the RTIL $[C_2mim][NTf_2]$. The response of HKUST−1/GC electrode in the presence of hydrogen was four times higher than a pure Pt electrode under similar conditions (Figure 1. Hydrogen appeared to become trapped in the pores of the MOF structures. This study highlights the successful application of cost-effective pristine MOF thin-films in combination with RTILs for low-cost gas leak-detection applications.

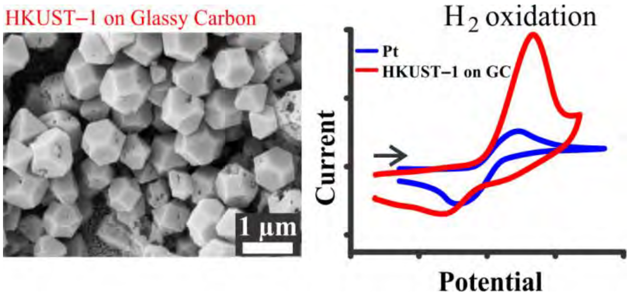

Figure 1. (left) Scanning electron microscopy image of the electrodeposited MOF, HKUST-1, on a glassy carbon electrode, (right) Cyclic voltammetry for hydrogen oxidation in an ionic liquid on the HKUST-1 modified GC electrode (red) compared to a conventional noble metal (Pt) electrode.

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Organic electrodes For Energy Storage and Conversion

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Organic electrode materials are attracting extensive attention, because they offer new possibilities for high energy/power density, cost-effective, environmentally friendly, and functional rechargeable batteries.[1] Charge storage of organic compounds involves an n-type doping/de-doping mechanism (e.g., the reversible enolization C=O ⇌ C-O-M, where M is a small electrolyte cation such as Li^+, Na^+, or K^+) and/or a p-type doping/de-doping mechanism (e.g., the redox reactions accompanied by the reversible adsorption/desorption of large electrolyte anions).

In this talk, we will introduce our recent work about charge storage characteristics of organic electrode materials, including the electrode kinetics, electrochemical stability, chemical stability, and de-solvent at interface. According to these characteristics, we design the organic based aqueous Li (or Na) ion battery with a super-long life of 50,000 cycles, [2-3] organic based Mg (or Zn) ion aqueous battery for grid energy storage, [4-7] organic based battery operated at -70 °C,[8-10] and the new application of organic electrode as proton buffer electrode for decoupled water electrolysis.[11,12] Finally, the challenge and opportunity of organic electrode materials will be briefly discussed.

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Model-assisted Analysis of Kinetics and Transport in Porous Electrodes by Species Frequency Response Analysis

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Numerous interacting processes affect electrochemical reactions at technical electrodes. Mass transfer, reactions and double layer charging are strongly coupled, which makes the quantitative description of porous electrodes a challenging task. Therefore, a thorough understanding of the transport and reaction phenomena is indispensable for designing better electrodes and processes.

Dynamic techniques such as electrochemical impedance spectroscopy (EIS) are often used to disentangle the individual processes and gain a better understanding. However, not all processes can be identified by EIS. In such cases, additional information may be obtained by recording further quantities besides current and potential.

In this work we present a new method to observe the dynamics of the transport of volatile species in porous electrodes during electrochemical reactions in addition to current and potential. We call this technique species frequency response analysis (sFRA). Model-based analysis is used to extract transport and kinetic parameters from the experimental results.

We demonstrate the capabilities of the new method by investigating the electrochemical methanol oxidation reaction on a porous Pt/Ru electrode. Differential electrochemical mass spectrometry is used to measure the dynamics of current, potential and the flux of the gaseous reaction product CO2. A one-dimensional mathematical model of the processes in the electrodes is developed and employed to analyse the transfer function that relates current density with CO2 flux.

We show how reaction and transport phenomena can be separated in the sFRA Nyquist plot by the model-based analysis. Effective electrode transport parameters and kinetic parameters are determined and we demonstrate that particularly transport parameters can be estimated with a better sensitivity by sFRA than by EIS.

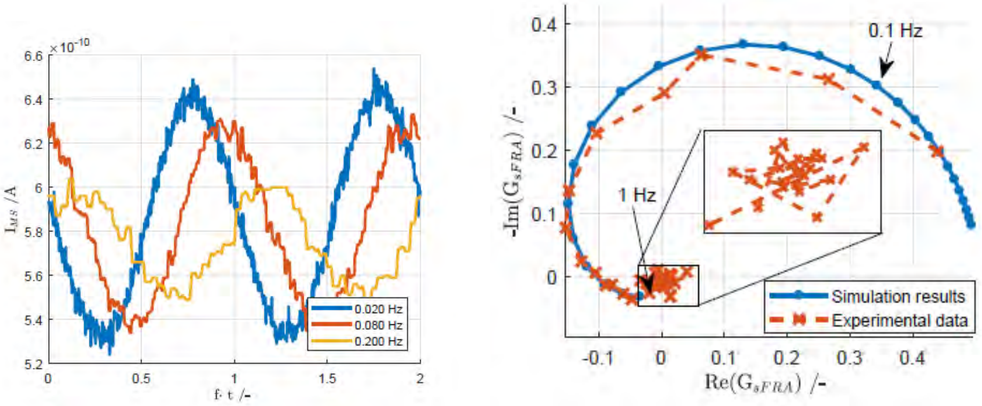

Fig. 1 Left: MS Signal over normalized time during sFRA measurement. Right: Nyquist plot of the sFRA spectrum [1].

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Electrochemical reactivity of *S*-Phenacyl-O-Ethyl-Xanthates in hydroalcoholic (MeOH/H_2O 4:1) and anhydrous acetonitrile media

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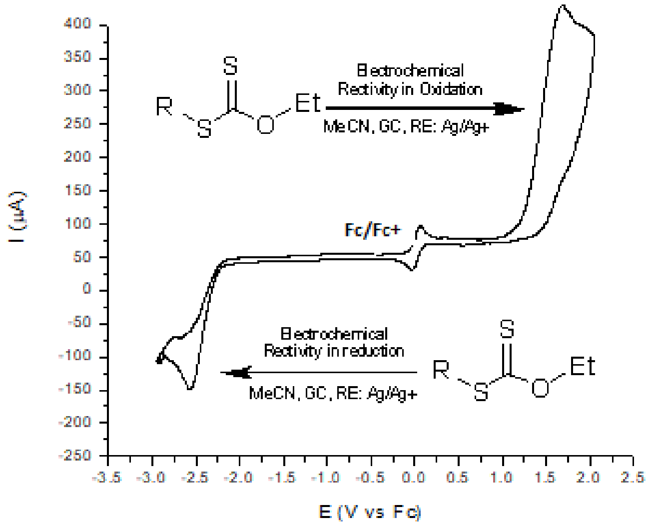
The electrochemical behavior of a series of *S*-phenacyl-O-ethyl-xanthates (O-ethyl-dithiocarbonate acetophenone derivatives) in hydroalcoholic (MeOH/H_2O 4:1) and anhydrous media (ACN_{anh}/$TBAPF_6$) using carbon electrodes was studied. Cyclic voltammetry showed in hydroalcoholic media only two cathodic waves, whereas in ACN_{anh} one anodic and two cathodic waves were present. The first cathodic wave corresponded to the reduction of the phenylketone group, whereas the first anodic was attributed to the xanthate unit. Macroelectrolysis on graphite and vitreous carbon at anodic and cathodic potentials, let us to explore the synthetic potential of this electrochemical reactions. With some compounds in hydroalcoholic media and using carbon electrodes, polymeric material was deposited on the electrode impeding the reaction; this deposit was characterized by AFM and SEM-EDS. The electroreduction on Ti electrode overcome this problem and gave the corresponding acetophenones (>95%). On the other hand, in ACN_{ahn}, small quantities of the dimeric 1,4-dicarbonyl compounds X-$PhCOCH_2CH_2COPh$-X (7-15%), as well as the corresponding acetophenones (*ca.* 50%) were isolated. Oxidation macroelectrolysis showed a very complicated transformation without synthetic value. The reaction mechanism for the reduction and the homolytic dissociation into the phenacyl radical was confirmed by DFT calculations.



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Liquid/liquid interfaces: a new platform to prepare and process thin films of complexes and multi-component electroactive materials

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This work aims to present a novel, simple and efficient strategy to both synthesize and process complexes and multi-component electroactive materials as thin films, developed by our research group, based on the interface between two immiscible liquids [1-10]. This one-pot and single-step methodology takes advantage of the high interfacial energy at a liquid/liquid (L/L) interface to induces a spontaneous self-assembly of different solids, as a thin film (few nanometers in thickness) that can be easily deposited over different kind of substrates, plastics included. The technique allows the deposition of high homogeneous thin films of electroactive single- or multi-component materials (as different nanocomposites) that cannot be deposited using conventional routes. Here, we will present the fundaments of the liquid/liquid interfacial route (LLIR) to thin films, and demonstrate several examples of preparation and application in different fields. Films of carbon nanotubes- or graphene-based nanocomposites with conducting polymers [1-5], oxide/hydroxide nanoparticles [6-8] or Prussian blue analogues [9-12], as well as nanocomposites of 2D materials-based nanocomposites (as MoS_2 [13] or black phosphorous [14]) will be demonstrated, and their application as high-performance active components in transparent and flexible electrodes [4], transparent Na- [12,13] and K-ion [3,9] or alkaline [7,8] batteries , supercapacitors [2], electrochromic materials [1,5,9], photovoltaic devices [5,11], electrodes for HER, electrochemical sensors [1,7], among others, will be discussed.

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Redox-enabling the electrical double-layer: redox-electrolytes vs. redox-materials

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Ion electrosorption, in combination with highly porous carbon electrodes, enables high power energy storage and recovery. As our understanding of the delicate nature of the electrical double-layer has improved, and with the use of advanced electrolytes with increased voltage stability, electrical double-layer capacitors have seen an increase in performance metrics. However, the charge storage capacity is fundamentally limited when excluding charge-transfer processes.

A straightforward approach is the compounding of carbon wit ha redox-active material (mechanical mixing). Electrodes based on composite materials are an easy way to transition from supercapacitor to battery seamlessly and allows cost-effective technology hybridization. The optimization must carefully consider material properties and performance metrics. For example, lithium manganese oxide benefits from a composite with activated carbon while lithium titanate already provides fast charge/discharge metrics to such an extent that no real benefit is gained from composite electrodes.[1, 2]

Another approach is the implementation of redox-active materials at the fluid/solid interface – basically, via nano-decoration of carbon surfaces with, for example, metal oxide materials. We discuss the benefits (and limitations) of doing so with advanced technology (esp. atomic layer deposition). In particular, the choice of carbon and its pore architecture is a crucial aspect of material hybridization.[3-7]

Finally, instead of using a solid/solid material combination, redox-activity can also elegantly be unlocked by combining highly porous carbon with redox-active electrolytes. The latter may contain a fluid/solid transition (electrodeposition), or the redox-ions may remain dissolved in the electrolyte during the entire charge/discharge process. Again, the carbon pore architecture is an important aspect to consider in addition to mitigating ion shuttling (which may cause rapid self-discharge).[8-10] Yet, the synergy of fast charge transfer and enhanced charge storage capacity accessible with redox-electrolytes make them a desirable domain for beyond-EDL-systems.

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Strategies for enhancing Corrosion Protection by Organic Coatings

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Organic coatings are an important pillar of corrosion protection. Usually they are mainly viewed as passive barriers that prevent the access of corrosive species to the metal. However, they often have also an active function, as they often contain active pigments that can release corrosion inhibitors. For high passive delamination resistance, usually the metal has to be pretreated prior to application of the organic coating, e.g. by phosphating, in order to prevent cathodic delamination, which is the fastest delamination mode. The main function of such conversion coatings is to impede electron transfer to oxygen that has to diffused through the coating the interface between coating and metal. Novel approaches how inhibit cathodic delamination without use of any conversion layers will be discussed. Concerning active protection by organic coatings the focus of current research is on so called self-healing coatings, often also referred to as smart or intelligent self-healing coatings. For realizing such intelligent coatings showing high level self-healing performance the design strategies differ from those that have to be followed for achieving optimum passive performance. The basic principles of passive and active performance will be highlighted in detail and implications for developing novel strategies will be discussed and latest research examples will be presented.

Electrolyte Influence on the Electrochemical Oxidation of Terbium and its Stabilization in Aqueous Media

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Lanthanides are used in various applications such as luminescent materials, magnets, catalysts, MRI reagents and (radio-)pharmaceuticals. Characteristic of their chemistry is the dominance of the trivalent oxidation state. As the 4f subshell is filled with electrons that are shielded by 5s and 5p electrons, 4f electrons are not participating in ligand interactions and chemical bond formation, resulting in similar chemical properties across the lanthanide series. The combination with their variable nuclear properties inspired their use in the field of nuclear medicine.

Apart from the generally dominant trivalent oxidation state, several lanthanides can occur in other oxidation states as well. For example, Sm, Eu and Yb have a relatively stable divalent state. Among these lanthanides, Eu(II) shows higher stability compared to Sm(II) and Yb(II) in aqueous media. There are several studies on the reduction of Eu by using either chemical, electrochemical or photochemical techniques for subsequent use in lanthanide separation. Whereas the most common electrolyte used in the reduction of Eu is chloride, recently reduction and stabilization of Eu(III) was achieved in concentrated nitrate media as well [1]. On the other hand the tetravalent state is well established for Ce ($E^0 = +1.72$ V vs. SHE), both in the solid state and in solution. Besides Ce, Tb ($E^0 = +3.1$ V vs. SHE) can also be oxidized to its tetravalent state, for example in mixed valence states in its oxide form. However, there is limited information on the oxidation of Tb(III) besides that it can be stabilized in concentrated carbonate solutions [2].

In this study, the oxidation of terbium is investigated via electrochemical methods. Tb(III) is oxidized in carbonate media via bulk electrolysis and the Tb(IV) product is identified via UV-Vis spectroscopy. A detailed parameter analysis is done to gain further insight in the reaction rate, stability and pH sensitivity of Tb(III) oxidation. Additionally, Tb(III) is oxidized in different electrolytes such as periodate and nitrate. Among all electrolytes the oxidation and stabilization is found to be the most efficient in concentrated carbonate solutions at relatively high pH. In addition, the kinetics of the Eu(III)/Eu(II) redox couple are studied using a rotating disc electrode. The gained insight in Eu(III) reduction in nitrate and chloride media, could also improve our understanding of Tb(III) oxidation. Once full control is achieved over the Tb(III) oxidation process, it could be applied in the separation of Tb from other lanthanides.

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Revising the Proton-Coupled Electron Transfer of Immobilized Hemin

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The combined study of the redox and acid/base properties of iron porphyrins is important to understand the effect of both the oxidation state of the metal center and the ionization state of the acid/base groups on the coordinative chemistry of heme.[1] In general, the interfacial electron transfer of metalloporphyrins is coupled to protonation / deprotonation processes involving their ionizable groups,[2] aimed at stabilizing one of the redox states involved in the process. Quantification of these proton-coupled electron transfer processes in hemin is useful to identify the molecular factors that control the redox potential of hemoproteins, and to rationalize the conformational changes induced by the exchange of ionizable ligands.[3]

Motivated by the discrepancy of the titration curves reported in literature for hemin immobilized onto graphite electrodes, we have revisited the effect of the solution pH on its voltammetric features. It has been found that its proton-coupled electron transfer is accompanied by binding events with the commonly used phosphate and acetate buffers that provoke significant deviations from the $1e^-/1H^+$ transfer expectations in the acid region. It is shown that these bindings involve the oxidized aquo-hemin complex and the ionized forms of the buffer, so that they are restricted to the pH interval where these particular forms coexist. A theoretical expression has been derived for the pH dependence of the redox potential taking into account the binding and acid/base speciation of the relevant species. Theoretical titration curves are characterized by an intermediate plateau, whose onset and extent vary with the buffer concentration in a similar way to that found experimentally. Fit of the theoretical expression to the experimental voltammetric titration curves allowed us to quantify the pK_a value of the iron-bound water molecule (3.85) as well as the hemin-acetate and hemin-dihydrogen phosphate binding equilibrium constants ($1.1\cdot10^4$ and $6.4\cdot10^3$, respectively), that reveals a greater affinity of hemin for the acetate anion than for dihydrogen phosphate. The negligible binding of hemin to the monohydrogen phosphate dianion is ascribed to both i) the electrostatic repulsion with the negatively charged propionate residues of hemin and ii) the low population of the aquo-hemin complex, since most of the water ligand has been replaced by hydroxide in the pH region of coexistence with monohydrogen phosphate.

Overall, this work provides a more complete speciation of immobilized hemin than previously considered, showing the substitutional lability of the aqua ligand in the oxidized state of the iron center and the reluctance of its hydroxyl counterpart to participate in an anion exchange with the buffer components.

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Smart Electrochromic/Thermotropic Windows of Energy-Efficient Buildings based on Different Electrolytes

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Progress, economic growth, and well-being depend critically on energy. To meet environmental challenges and to address the energy demand of future generations, a global energy technological transition based on low-carbon alternatives and renewable sources is urgent. The ultimate target is to guarantee affordable, reliable, safe and universal access to energy. At least part of the energy solution lies in the building sector which accounts for about 40% of the primary energy use and related greenhouse gas emissions. Modern buildings use energy to provide occupants with thermal (heating, cooling and ventilation) and visual (lighting) comfort, and to power major appliances. Windows, a component of the buildings envelope, offer key opportunities in terms of energy saving, as they are responsible for ca. 10% of the total energy consumed in the building. The development of dynamic windows enabling the control in real time of sunlight transmittance (visible radiation) and solar heat gain (near-infrared (NIR) radiation) to internal or external conditions, or to the occupant's choice, and adapted to all types of climates, is extremely attractive. In particular, electrochromic windows have huge potential to reduce energy use, increase indoors thermal/visual comfort, and improve outdoors view [1].

Device systems with an archetypal five layer configuration comprising cathodically coloring tungsten oxide (WO_3), anodically coloring nickel oxide (NiO), two visible- and NIR-transparent conductive oxide layers (amorphous indium zinc oxide (a-IZO) [2-4] and indium molybdenum oxide (IMO) [5]), and an electrolyte layer were assembled. Three classes of electrolytes differing in the nature of the host matrix, dopant species, and synthesis procedure, were investigated: (1) Hybrid polymer/siloxane electrolytes prepared by the sol-gel process and doped with a protonic ionic liquid [2], a mixture of lithium and erbium salts [5], or a mixture of a lithium salt and an erbium complex [5]; (2) Polymer electrolytes composed of seaweeds-derived k-carrageenan polysaccharide and an erbium salt [3]; (3) Non-Newtonian nanofluid electrolytes based on glucose-derived carbon dots functionalized with a thermotropic ionic liquid [4,6]. The three electrolyte design strategies adopted resulted in sustainable electrochromic [2,3,5], thermotropic [4,6] or integrated thermotropic/electrochromic [4] devices with outstanding performance.

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Powering Catalysis and Growth in Microorganisms Using Electrochemistry and Synthetic Biology

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Microorganisms precisely control biological processes, including biosynthesis and cell growth, by regulating the redox state of different biomolecules. These processes can be modulated by electrochemically coupling intracellular biomolecules to an external electrode, but current approaches afford only limited control and specificity. Here we describe using electrical current to reduce specific biomolecules, allowing control of biosynthesis and cell growth in two industrially relevant microorganisms, *Escherichia coli* and *Lactobacillus plantarum*.

To enable electrochemical control of *E. coli*, we used synthetic biology to introduce a heterologous electron transfer pathway. *E. coli* expressing *mtrCAB* from *Shewanella oneidensis* MR-1 consumed electrons directly from a cathode when fumarate or nitrate, both intracellular electron acceptors, were present. The fumarate-triggered current consumption occurred only when fumarate reductase was present, indicating all the electrons passed through this enzyme. Moreover, MtrCAB-expressing *E. coli* used current to stoichiometrically produce ammonia. Thus, our work introduces a modular genetic tool to reduce a specific intracellular redox molecule with an electrode, opening the possibility of electronically controlling biological processes such as biosynthesis and growth in any microorganism.

Complementing this approach, we discovered that *L. plantarum*, a lactic acid bacteria used industrially to produce fermented foods, can uptake electrons. This electron uptake occurs under anaerobic conditions when a terminal electron acceptor and its corresponding oxidioreductase are present. Unlike other anaerobic respiratory modes in *L. plantarum*, this current consumption does not require addition of co-factors such as heme or riboflavin. Electron uptake promotes cell growth and acidification of the media, both processes essential for food fermentation. We find that the *L. plantarum* metabolism is shifted towards ATP producing pathways in the presence of both a cathode and a suitable electron acceptor. This surprising discovery opens the possibility of using electrical current to drive industrial production of fermented foods using lactic acid bacteria.

A Voltammetric Study of Nitrogenase Catalysis Using Electron Transfer Mediators

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The selective reduction of N_2 to NH_3 is a major challenge for industrial, biological, and synthetic chemistry.[1] In nature, the enzyme nitrogenase catalyzes the nitrogen reduction under mild conditions.[2] The molybdenum-dependent nitrogenase consists of two component proteins (Figure 1a): the molybdenum-iron protein (MoFeP) and the iron protein (FeP). MoFeP houses two unique cofactors, the electron carrier [8Fe-7S] (P-cluster) and the catalytic [7Fe-9S-1Mo-C-homocitrate] (FeMo-co). FeP contains a single [4Fe-4S] cluster and two MgATP binding sites. During the catalytic cycle, the FeP is reduced either by flavodoxin or ferredoxin (*in vivo*), or sodium dithionite or reduced methyl viologen (*in vitro*), and binds two MgATP molecules. Then FeP transiently associates with the MoFeP, transfers an electron followed by hydrolysis of two MgATP molecules and dissociation from MoFeP. The released oxidized FeP is reduced, the two MgADP are replaced by two MgATP, making FeP ready for another round of MoFeP reduction. In the presence of N_2, this cycle (called the FeP cycle) is repeated eight times to achieve the reduction of the N_2 to two ammonia molecules (eq 1). In the absence of N_2, nitrogenase catalyzes the reduction of protons to H_2 (eq 2).

$$N_2 + 16\ \mathrm{MgATP} + 8\ H^+ + 8\ e^- \rightarrow 2\ NH_3 + H_2 + 16\ \mathrm{MgADP} + 16\ P_i \qquad (1)$$

$$4\ \mathrm{MgATP} + 2\ H^+ + 2\ e^- \rightarrow H_2 + 4\ \mathrm{MgADP} + 4\ P_i \qquad (2)$$

In this study, a mediated cyclic voltammetry approach was developed that provides a quantitative analysis of electron flow through nitrogenase.[3] Conditions were optimized to reveal the catalytic reaction rate-limiting step. Analysis of the current response by an electrochemical approach yielded a catalytic rate constant (k_{cat}) of 14 s^{-1}, consistent with earlier studies. The current approach was used to resolve a long-standing conundrum in nitrogenase research, the apparent inhibition of electron flow through nitrogenase with increasing partial pressures of N_2. It was demonstrated using this voltammetric approach in the absence of the reductant dithionite that total electron flow through nitrogenase remains constant up to an N_2 partial pressure of 1 atm.

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Scalable biofilm electrodes

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Bioelectrochemical systems (BESs) suffer from scale-up limitations. This is one of the major bottlenecks preventing the utilization of technology in practical applications. For example, Figure 1 shows how maximum current density changes with anode surface area in microbial fuel cells. It is clear that the current density is negatively correlated with electrode surface area. There have been many attempts to show scalability and improve current densities in BESs. However, most of systems reporting high current density when impractically small electrodes are used or in short term operations. It is possible to observe a higher power generating (or consuming) BESs in short term due to the capacitance of the electrodes. However, this is not practical. Previously our group published several research papers on scalability of BESs. Our recent works mainly focused on polarized biofilm electrodes and their scalability. We hypothesized that scalability of biofilm electrodes is controlled by mass transport. In this presentation, we summarize our recent work on the scalability of biofilm electrodes and the effect of substrate concentration on the current density of anodic and cathodic biofilm electrodes. We concluded that biofilm electrodes can be linearly scaled under controlled conditions, and we suggest a framework for scaling up BES for practical applications.

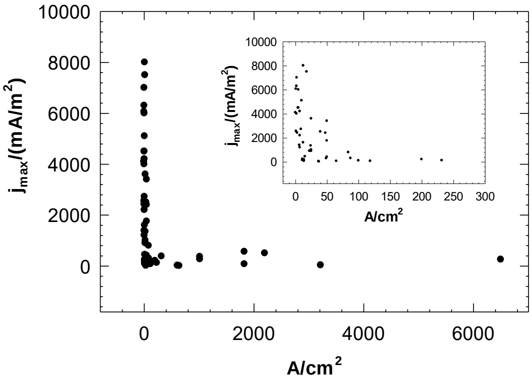

Figure 1. Maximum current density versus anode surface area. The inset shows the data for smaller anode surface areas. The data demonstrates that the bioelectrochemical systems scale at significantly low current densities.

Designing interphases for lithium, zinc and aluminum anodes

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The ever-growing demands of portable electronic devices accelerate the development of energy storage/conversion devices with high energy density.[1] Rechargeable metal batteries, applying high capacity and reactive metals (Li, Na, Zn, Al *et al.*) as anodes have been recently paid increasing attentions due to their high specific capacities (*e.g.* ~3850 mAh/g for Li) that are ten times higher than traditional graphite anode.[2] However, comparing with the graphite anode, the solid electrolyte interphases (SEI) formed on metal anodes are not stable, resulting in low Coulombic efficiencies of metal plating/stripping, and irregular shapes of metal deposition.[3,4] In specific situation, the growth of metal can even lead to a dendrite like structure, which shows potential risk to penetrate the separator and cause short circuit of batteries.

Various approaches have been developed to build stable interphases on metal surface, such as modification of electrolytes, preparation of 3D host for metal deposition, design of artificial SEI.[2] Here some emerging feasible strategies will be discussed to build stable interphases on metal surface, not only for lithium metal but also for other low cost metals such as Zn and Al.[5-7] In particular, for Zn and Al, the growth of metal can be orderly arranged by an interphase that shares similar crystal structures with deposited metal, named as epitaxial growth. Meanwhile, the demand of solid electrolyte interphase is different for various metals. For example, the Al metal naturally possesses a dense and high band-gap oxide layer, leading to sluggish kinetic of Al stripping. The design of ionic liquid based interphase on Al surface can replace the original oxide layer and facilitate the kinetics of Al anode.

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Capacitive Performance of Polyaniline Modified Conductive Bacterial Cellulose as Anode in Supercapacitive Microbial Fuel Cell

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Microbial fuel cell (MFC) is a developing technology for producing bioelectricity from organic compounds of waste materials that has cough the eye of scientists in recent years. In MFC, microorganisms as active biocatalysts decompose organic matters to electrons and protons [1]. Electrons by the anode as electron acceptor and by external circuit are transferred to cathode electrode to take part in oxygen reduction reaction. In spite of low cost feed in MFC, this technology is not still economic. Electrode materials are the high cost compartments of MFC. To decrease the cost of this technology, using low cost material is a solution[2]. Furthermore, exploiting the supercapacitive features of the MFC has been demonstrated a viable solution to boost power performance of supercapacitive MFCs [3]. Bacterial cellulose (BC) as a cheap biopolymer has been exploited as a flexible substrate for electrode fabrication. It is a porous media hydrogel pure cellulose produced by *Acetobacter* [4]. In this work, BC was coated by carbon nano tube (CNT) to become conductive and then coated electrochemically by polyaniline (PANI). It was used as anode in MFC. PANI as a conductive polymer has been utilized as anode modifier by the scientist[5]. In this research the capacitance behavior of PANI modified BC-CNT was studied before and after biofilm formation and also was compared with the effect of biofilm on BC-CNT's capacitance. For this purpose, impedance spectroscopy is a useful method which was run in the MFC. The results showed that for BC-CNT, the capacitance was decreased after biofilm formation while for the PANI modified electrode the capacitance was increased. Moreover, cyclic voltammetry and galvanostatic discharging demonstrated higher capacitance of PANI modified anode after biofilm formation. Additionally, power density of MFC showed higher performance of modified anode. Finally, FESEM images showed higher biocompatibility of PANI modified anode by higher density of formed biofilm on electrode surface. As a result, the PANI modified bioanode provided an active biofilm and resulted in higher capacitance which was verified by different electrochemical methods.

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The Electron as a Probe to Measure the Thickness Distributions of Electroactive Films

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Electron conducting films are ubiquitous in applications such as energy conversion, and their ability to fulfil their catalytic function can be greatly limited by inhomogeneities in their thickness or breaks within the film. Knowing the electroactive film thickness distribution would greatly facilitate optimization efforts, but techniques to measure this are lacking. Here, we present an electroanalytical method that provides the thickness distribution of the electrochemically accessible fraction of redox-active films in which the transfer of electrons is diffusional, i.e. by electron hopping. In this method, as the time scale of the experiment (the scan rate) is changed, the location of the diffusion layer boundary relative to the film roughness features is varied, allowing for the extraction of the film thickness distribution. In addition to being conveniently carried out in the solvated state, which is often the operational state of these conductive films, this approach is highly complementary to classical microscopy methods since it samples the entire modified electrode and is specific to the electroactive portions of the film. Therefore, this approach provides information on film morphology that is truly relevant for the catalytic processes being optimized, and thus can guide the optimization of catalyst integration in films towards macroscale cohesion and thickness homogeneity which are essential for optimal performances. The results of this research have recently been published[1], and are relevant to conditions of reversible electron transfer. Efforts are currently underway to extend the model to include quasi-reversible and irreversible electron transfer kinetics.

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Effect of the Synthesis Parameters of in situ growth LDHs on the filiform corrosion susceptibility of painted AA5005

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AA5005 is an aluminum alloy whose main alloying element is Mg. This alloy is employed for constructions, furniture, packaging, in the chemical industry and marine structures. These applications often involve the exposure to aggressive environments: for this reason, very often an organic coating is applied to extend the service life of the structure/manufacture. Among the different failure mechanisms which are responsible for the reduction of the service life of painted aluminium sheets, filiform corrosion frequently occurs in humid and saline environment. Filiform corrosion, which consists in small threadlike delamination tracks driven by differential aeration conditions, usually triggers from surface defects in the protective film in the presence of soluble ionic species in presence of a r.h. between 50 and 90% and relatively high temperature.

Among the different chemical conversion treatments of the aluminium substarte which can be employed to reduce the filiform corrosion phenomenon an alternative can be the use of Layered Double Hydroxides (LDHs) grown in situ over the AA5005. In this study, the effect of the synthesis parameters of Layered Double Hydroxides (LDHs) based thin layers on AA5005 is investigated in order to develop a filiform corrosion resistant solution. LDHs consist in a class of synthetic anionic clays having a layered structure based on magnesium hydroxide (brucite, $Mg(OH)_2$). LDHs are currently studied for different applications, such as additives in functional polymeric materials, as a mean for water decontamination, as osmotic membranes for water desalination and also for exchange and ionic species by absorption. In this work, Al/Mg based LDHs have been developed in autoclave under different synthesis conditions: the effect of the synthesis time and urea presence have been investigated. The morphology of the developed LDH layer have been investigated by SEM and AFM. The thickness and the structure of the developed coatings have been assessed by FIB-SEM. XRD pattern have been collected over the sample to check the LDH structure and to characterize the interplanar distance obtained by playing with the different synthesis parameters. The corrosion protection properties of the as synthetized layers have been investigated by means of polarization curves and electrochemical impedance spectroscopy (EIS).

In the second stage of the work, an epoxy clearcoat has been applied over the AA5005 plates covered by the different LDH layers (in terms of morphology, thickness and composition). The effect of the different LDH layers on the filiform corrosion susceptibility has been assessed in compliance with the ASTM D2803 − 09 standard. The effect of the different surface condition on the formation of filiform filaments has been unravelled.

Free Charge Density Gradients in Room Temperature Ionic Liquids and The Factors that Control Them

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Free charge density gradients that extend over macroscopic distances (*ca*. 100 μm) have been seen in room temperature ionic liquids (IL). These gradients, the magnitude and sign of which is controlled by the surface charge of the support on which a film of ionic liquid resides, can be controlled in both magnitude and spatial extent by the molecular structure and organization of IL systems. Our recent work has demonstrated the ability to quantitate the magnitude of the gradient using molecular diffusion measurements. Both the structures of the IL constituents and the presence of diluent affect the gradient in a predictable manner. Current work is focused on identifying the best way to model these systems and devising nonlinear optical spectroscopic strategies for characterizing the charge density gradient.

Electrochemical Approach to Durability of Reinforced Concrete Structures

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The Eurocode-2 “Design of concrete structures” approved in 2004 introduces the concept of durability for construction works. Several parameters related to the mixing compositions or to the safety levels for chloride content are defined, that need of reliable methods for correct assessment of the structure’s integrity.

Corrosion of reinforcing steel bars is recognised as one of the main factors involved in the durability concept, which brings to the need for developing techniques and procedures able to assess corrosion initiation and development. The corrosion potential and polarization resistance are the main electrochemical techniques considered for on-site inspection, under the assumption that the cathodic process corresponds to oxygen reduction and the anodic process to steel corrosion. Although these assumptions are mostly true, they are not able to explain some transitions from passive to active states, as well as some corrosion potential evolutions.

This talk will review recent achievements in understanding the electrochemical response of the steel-concrete interface with the aim of evaluating the possibilities of the electrochemical impedance spectroscopy technique (EIS) for providing quantitative information on the rebar’s corrosion process, and also on the transport of aggressive ions through the concrete cover, thus dealing with durability assessment issues.

Multielectrochromic Conjugated Polymers Based on 2,5-Di(thienyl)pyrrole Derivatives

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Among various π-conjugated polymers described in the literature, a 'trimeric' π-extended system based on thiophene bonded to a central pyrrole moiety, namely 2,5-dithienylpyrrole (SNS), has receiving a great deal of attention, since its correspondent polymer can be obtained either by chemical or electrochemical polymerization [1,2]. Furthermore, the oxidation potential of the monomer is less anodic when compared to pristine pyrrole or thiophene and the so-obtained polymer films show multielectrochromic response [3,4]. 2,5-di(thienyl)pyrrole derivatives bearing dansyl (SNSD) or fluorene (SNSF) substituents were prepared by simple synthetic routes, and successfully electropolymerized or copolymerized with 3,4-ethylenedioxythiophene (EDOT) on ITO electrodes by using tetrabutylammonium tetrafluoroborate ($(C_4H_9)_4NBF_4$) / acetonitrile (CH_3CN) as electrolyte. The electrochromic properties of the so-produced polymer films, P(SNSD-co-EDOT) and PSNSF, were investigated by spectroelectrochemical techniques. P(SNSD-co-EDOT) films deposited on ITO with 1:5 feed ratio presented multielectrochromism with rainbow-like colors depending on the applied potential, whilst PSNSF films shows color variation from yellow in the neutral state to green and blue in the oxidized state, as can be seen in the track of the CIE 1931 *xy* chromaticity coordinates, Figure 1. Both polymer films also presented high absorption in the near infrared region, chromatic contrast (Δ%T) in the range of 11 – 40 % depending on the λ, coloration efficiency (η) from 110 to 350 cm^2 C^{-1}, fast switching time (< 1.0 s), and stability to redox cycling. Such properties make these materials potentially applicable as active layer in optoelectronic devices.

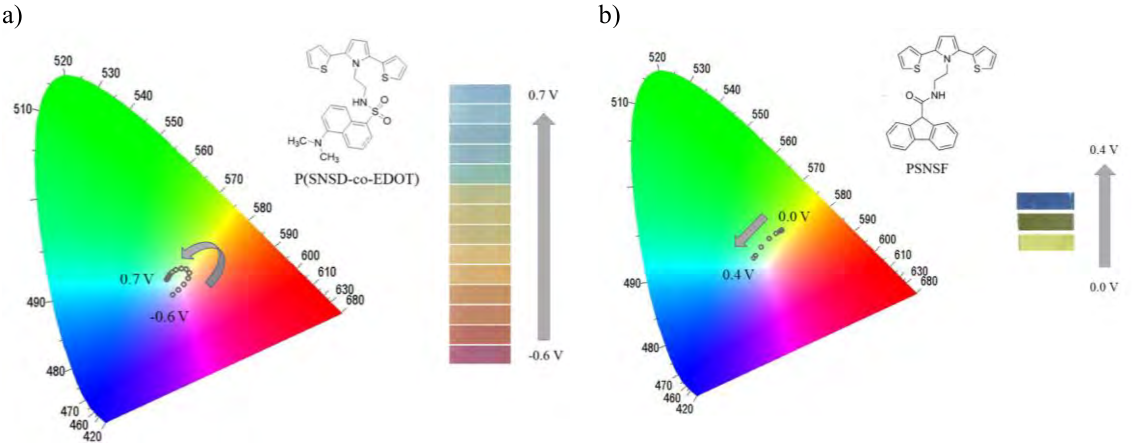

Figure 1. Calculated colour trajectory in the CIE 1931 color space and images of the a) P(SNSD-co-EDOT) film deposited on ITO with 1:5 feed ratio and b) PSNSF film deposited on ITO, registered during potential scan from -0.6 to 0.7 V and 0.0 to 0.4 V *vs.* Ag/Ag$^+$, respectively.

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Microbial Electrochemical Technologies: False Leads, Open Perspectives and Ethics

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For almost two decades, microbial electrochemical technologies (MET) have been opening up amazing perspectives in various application sectors: production of electrical energy from wastewaters, replacement of fossil fuels by bio-hydrogen, mitigation of global warming by the transformation of carbon dioxide into renewable fuels, etc. Basic knowledge on extracellular electron transfers and electroactive biofilms is growing rapidly, revealing fascinating aspects of microbial life but, in spite of great fundamental advances, the technological promises seem to be a very long way from being fulfilled.

The presentation points out some major bottlenecks that preclude the development of the large-scale MET applications that have been announced. This analysis shows that some initial leads are obvious dead ends. It also reveals research avenues that seem more reasonable (in the author's opinion).

First of all, as a basic principle, conventional electrochemical reactors require electrolytes of high ionic conductivity to be efficient. Designing electrochemical cells that should operate with urban wastewater, i.e. electrolyte with ionic conductivity commonly less than $0.5\ S.m^{-1}$, is consequently an unattainable challenge …at least in the absence of really groundbreaking concepts. An alternative that is sometimes evoked would consist in compensating for the poor efficiency of weakly conductive media by designing low-cost electrochemical reactors. Unfortunately, industrial electrochemical reactors are necessarily expensive and have to work at high current density to be economically efficient [1].

Saline and hypersaline electrolytes may offer interesting leads for the development of large-scale MET [3]. In this context, analysis of ion fluxes shows that increasing salt concentrations results in reduced mitigation of the bioanode acidification, which is a severe inhibiting step [4]. This should be a major research axis to be explored. When the objective is no longer to produce electrical energy or to perform electrolysis, but to treat effluents or to enhance some microbially-catalyzed redox reactions, possible low-cost MET options such as microbial snorkel [2] or interspecies electron transfer mediated by conductive particles, can be regarded with hope, even for implementation in media of low ionic conductivity.

Scaling-up MET for CO_2 reduction is definitively hampered by the proximity of the reduction potentials of CO_2 and water. A microbial electrosynthesis cell working at high current density consequently results in the evolution of hydrogen, which peels off the biofilm from the cathode surface. Microbially-catalyzed hydrogenation carried out in two separate steps is a much more promising process configuration [5].

Finally, the question is raised as to whether we should feign ignorance of some obvious deadlocks and propose appealing but unrealistic applications to scientific policy makers in order to be able to continue our work in this exciting research field.

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Antibiofilm activity of dinuclear silver(I) complexes with pyridine-based macrocyclic type of ligand against clinically relevant species

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Electrochemical techniques allow monitoring of antimicrobial activity in early biofilms [1]. Biofilms of the unicellular fungal pathogen (*Candida parapsilosis* ATCC 22019) and a Gram-negative bacterium (*Acinetobacter baumannii* ATCC 19606) were grown on screen-printed electrodes (SPE) in potentiostat-controlled electrochemical cells and exposed to two dinuclear silver(I) complexes at a concentration equal to the minimum inhibitory concentration (MIC) determined against planktonic bacteria, in the presence of the exogenous redox mediator $[Fe(CN)_6]^{3-}$. $[Fe(CN)_6]^{3-}$ applied in this concentration (100 μM), does not block growth of the microbial biofilms at the concentration tested in this study, as appreciable current outputs, which depend strictly on biofilm growth, were obtained when the cells were grown in the presence of the redox mediator $[Fe(CN)_6]^{3-}$ only. The working electrode was maintained at constant electrochemical potential (0.4 V vs. Ag pseudo-reference electrode). Under these conditions, part of electron flow due to the oxidation of nutrient in the growth medium is transferred extracellularly to the electrode. We have previously shown that the instantaneous current output and the overall charge output after a defined time are correlated to the formation of the biofilm or its inhibition due to an antibiofilm agent in solution. Chronoamperometry (CA) results confirmed that complex 1 has antibiofilm activity against *C. parapsilosis*, as observed by the lower instantaneous current, while it has limited effect on the biofilm activity of *A. baumannii* (Fig. 1). This result also suggested that the minimum inhibitory concentration for biofilm is higher than that in the planktonic phase, being in accordance with the results obtained from the standard microtiter plate based in vitro assay. The CA for the other two strains did not show a well-defined pattern. The non-turnover cyclic voltammograms (CVs) at 0 h are similar with and without the antimicrobial complex 1, while the turnover CVs at 24 h in the presence of complex 1 is much lower than in its absence, as complex 1 affects the bacterial metabolism and reduces the extracellular electron transfer rate. The effect of complex 1 on biofilm formation was also determined through the crystal violet assay in this set up. The amount of biofilm on the working electrode was determined for *A. baumannii* and *C. parapsilosis* with crystal violet assay, which underestimates the attached biomass, due to the multiple washing steps [2]. Overall, electrochemical experiments show that much higher concentration of complex 1 is needed to exert a strong antibiofilm inhibiting activity, while the effect is observable at planktonic MIC concentration. The difference between the CA, CV and crystal violet assays shows that multiple analytical methods are needed to determine the true nature of the antibiofilm effect of a given antimicrobial agent.

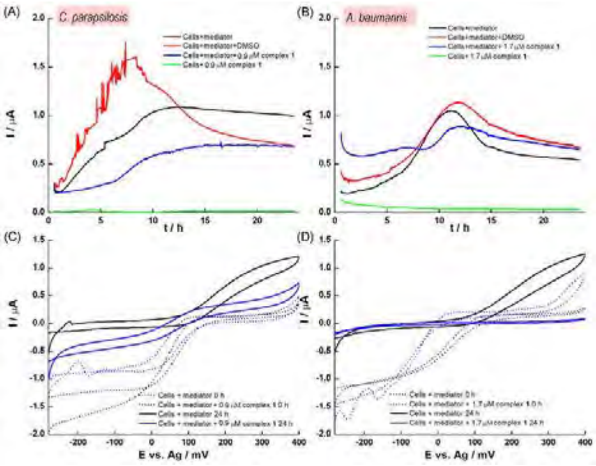

Fig. 1 CA of *C. parapsilosis* (A) and *A. baumannii* (B) biofilms in bioelectrochemical cells. Cells with $[Fe(CN)_6]^{3-}$ (black traces); cells with $[Fe(CN)_6]^{3-}$ and DMSO (red traces); cells with $[Fe(CN)_6]^{3-}$ and 0.9 or 1.7 μM of complex 1 in DMSO (blue traces). Cells with complex 1 in DMSO without $[Fe(CN)_6]^{3-}$ (green traces). CV of *C. parapsilosis* (C) and *A. baumannii* (D) at 0 h (dashed traces) and 24 h (solid traces). Cells with $[Fe(CN)_6]^{3-}$ (black trace); cells with $[Fe(CN)_6]^{3-}$ and 0.9 and 1.7 μM of complex 1 in DMSO (blue traces).

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Husbanding Biological Heat to Optimise Energy Conversion in Bioelectrochemical Systems (BES)

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Bio-electrochemical systems (BES) use bacteria as biocatalysts to decompose organic matter and generate electricity, in the case of Microbial Fuel Cells (MFCs), or generate hydrogen, in the case of Microbial Electrolysis Cells (MECs). Since the early 2000s, research around the subject has surged due to the capability of this technology to treat and convert wastewater into useful byproducts, i.e. green energy. To test the propensity of the technology in real world scenarios different pilot-scale studies have been deployed around the globe from different research groups.

These studies have shown that BES holds a great potential as a sustainable technology however, the performance of pilot scale studies (100-1000L) is 1-3 order of magnitude lower than the lab scale (0.1-0.2L) ones. Primarily the research towards addressing this disparity, has been focused for a long time on materials rather than the biology of the system itself. It has been observed that BES can show resilience and continue operating at temperatures below 20 ºC, where normal anaerobic sewage treatments struggle. Hence it is suggested that the heat energy produced during bioconversion of chemical energy to electrical energy is an important energy vector which has not been accounted for.

Thermodynamic calculations show that counter intuitively biological anodes when fed acetate in BES take in heat energy, i.e. they get colder, preliminary data shows this may be an observable phenomenon even in mixed cultures (Figure 1). However, the digestion of upstream substrates such as longer chain starches to glucose will produce heat, this was significant and measurable in 120L pilot scale study [1]. These data suggest that heat transfers are observable and substrate dependent. Further exploration of the thermodynamics, and in particular enthalpy, of the reactions involved in the anaerobic digestion of wastewaters is warranted.

Balancing the energy inputs and outputs will be important for the industrial credibility of BES technology. Additionally, linking heat energy to growth will offer deeper understanding of the biology of anaerobic systems. These are vital steps in the process of engineering efficient biological systems to extract energy, either through classical anaerobic digestion, or with BES. Through a new project (BIOHEAT), the authors will investigate the heat energy transfers in microbial systems in order that we are able to efficiently engineer and husband them.

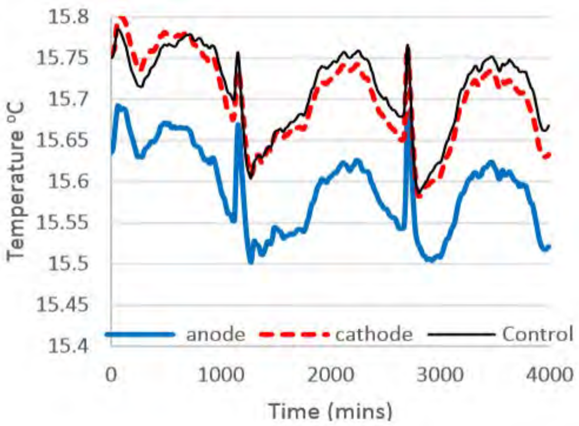

Figure 1 Measured temperature in a BES reactor fed on acetate.

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Recent Advances in Electrochemical Surface Oxidation-Enhanced Raman Spectroscopy.

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The enhancement of the Raman signal is fundamental to analyze molecules since it overcomes the low sensitivity of Raman spectroscopy. Usually, the Raman signal has been improved with plasmonic nanostructures using the Surface Enhanced Raman Scattering (SERS) effect. For many years, this phenomenon has been studied and, even today, some critical aspects are not fully understood. In 2018, our group discovered a new phenomenon that was denoted as Electrochemical Surface Oxidation Enhanced Raman Scattering (EC-SOERS),[1] because it only takes place during the oxidation of a silver substrate under specific conditions. EC-SOERS is an electrochemical phenomenon because, as far as we know, the enhancement of the Raman signal can only be obtained when an anodic overpotential or current is applied to the silver electrode. Therefore, this effect can only be studied using spectroelectrochemistry.

The enhancement of the Raman signal was initially observed during the oxidation of a silver substrate, in acidic medium with small amounts of chloride[2]. The origin of EC-SOERS still remains unclear; however, this phenomenon has been successfully used for quantitative analysis of different compounds[3], such as, uric acid, citric acid or caffeine. Moreover, EC-SOERS exhibits a high reproducibility and also a remarkable selectivity that can be used to resolve complex mixtures, as has been demonstrated in the quantification of vitamin B3[4]. The enhancement factors calculated for EC-SOERS indicate that not only a chemical effect but also an electromagnetic effect influences on the enhancement of the Raman signal. Therefore, some type of plasmonic nanostructures are being generated during the oxidation of the electrode.

In this communication, we show the latest developments achieved in the study and application of EC-SOERS. On the one hand, the structures of the molecules plays a fundamental role in the enhancement of the Raman signal. On the other hand, new electrolytic mediums can be used to improve the selectivity in the determination of different molecules. Moreover, this phenomenon has been observed in very different conditions, giving evidence of a more general phenomenon.

This work shows the most recent advances obtained in the study of EC-SOERS, a phenomenon similar to SERS, but with clear differences that can be used to analyze compounds that sometimes are not easily observed in SERS.

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Gold nanoparticles-hybrid nanostructures in electrochemical immunosensing of metastatic cancer and neurodegenerative diseases

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Nowadays, neurodegenerative disorders (NDD) and cancer diseases, due to their increasing prevalence and prolonged duration, pose a major global health problem for worldwide population, and a tremendous financial impact associated with medical care for families and society. Despite this, their early detection and follow up are complex tasks, usually performed by techniques, which, although being sensitive and reliable, show some limitations regarding their costs, assay time, invasiveness, complicated protocols and trained personnel for their execution or interpretation. Therefore, the development of low-cost and accessible methods, compatible with point-of-care technology (POCT), for quantifying closely related biomarkers is of great interest.

In this field, electrochemical immunosensors are flourishing as promising alternative tools for diagnosing, prognosing and characterizing this heterogeneous group of diseases, while meeting the POCT requirements: simple but high-performance devices, ensuring sensitive and selective analysis in non-laboratory environments and with limited resources, with easy-to-use equipment and minimal analysis time. The analytical performance of these biodevices can be considerably improved by means of rational surface chemistries such as the use of diazonium salts and/or the coupling with smart nanomaterials, like gold nanoparticles (AuNPs). The latter constitute one of the most widely used nanomaterial in single or multiple-component nanostructures and nanocomposites, due to their unique properties. AuNPs/multi-walled carbon nanotubes (AuNPs/MWCNTs) nanocomposites and dendrimer-encapsulated AuNPs are particularly attractive options to be exploited in electrochemical biosensing due to their remarkable conductivity, catalytic ability, biocompatibility and high density of active groups for biomolecules immobilization.

In this presentation, the most relevant aspects of pioneering use of AuNPs/MWCNTs [1] and AuNPs-poly(amidoamine) (PAMAM) dendrimer nanocomposites [2], prepared in the laboratory, as nanocarriers of multiple detector antibodies and peroxidase (HRP) molecules or electrode modifiers, respectively, in electrochemical immunosensing approaches recently developed to determine biomarkers of emerging relevance in metastatic cancer (Receptor Activator of Nuclear Factor-κB Ligand, RANKL) and neurodegenerative diseases (tau protein) will be critically discussed. These approaches are based on sandwich immunoassay formats and involve the use of commercial reagents and disposable electrodes modified by electrochemical grafting with 4-aminobenzoic acid (*p*-ABA) and amperometric transduction using the H_2O_2/hydroquinone (HQ) system.

The excellent characteristics that these AuNPs-based nanostructures impart to the resultant immunosensing platforms in terms of sensitivity, selectivity, and operational and storage stability for determining the target biomarkers in the required clinical ranges will be critically discussed. Moreover, their potential to direct and accurate determine the endogenous target biomarker levels in human serum, plasma and brain tissues samples from colorectal cancer or NDD-diagnosed patients, simply by placing a 5-µL drop of the undiluted biofluid or containing 2.5 µg of the tissue extract over the immunoplatform, and involving simple-handling and short turnaround protocols (1-2 h) will be presented.

Our recent experimental results confirm that these electrochemical immunosensors are competitive with commercial methodologies in terms of simplicity and assay time, which along with the amenability to be implemented in single or multiplexed formats and using affordable, low-power requirement and portable instrumentation, make them very attractive tools to further advance in the consolidation of candidate clinical biomarkers in metastasis and neurodegenerative processes, and their implementation in POCT devices to perform decentralized and rapid routine determinations.

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Towards Electrodeposition of InSb at the Nanoscale from Weakly Coordinating Solvents

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InSb is an infrared detector material which would have enhanced properties and tunability if deposited at the nanoscale. Electrodeposition provides a bottom-up approach to filling high aspect ratio nanostructured templates which conventional gas phase deposition can struggle with. Weakly coordinating solvents are useful for this purpose due to low surface tension and the solvent not affecting the electroactive species or any of the intermediates during electrodeposition.

The suitability of using tetrabutylammonium halometallate precursors in dichloromethane has been demonstrated for a number of p-block elements [1]. The electrodeposition of $Ge_2Sb_2Te_5$ [2] and Bi_2Te_3 [3] from this system has also been demonstrated. This presentation will cover the electrodeposition of InSb from this system at different length scales. The electrochemical behaviours of the precursors, the different challenges associated with producing and using templates at each length scale, and the composition control of the resulting deposits, will be highlighted.

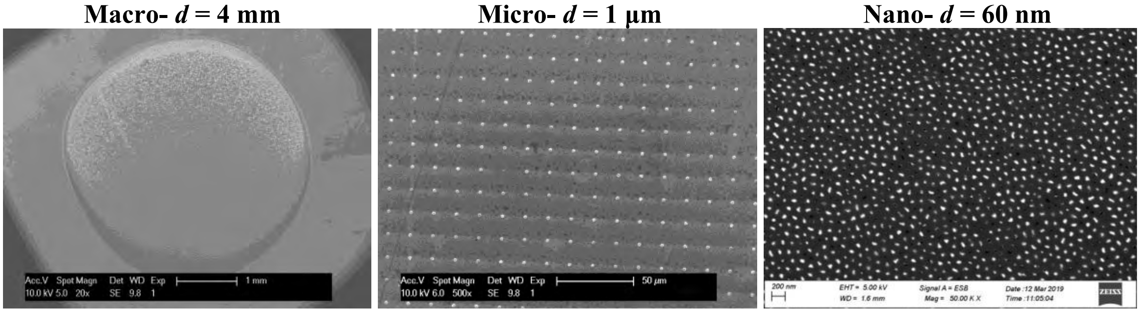

Figure 1: SEM images of InSb electrodeposits at different length scales

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Proton Coupled Electron Transfer Catalysts.
Principles and Applications

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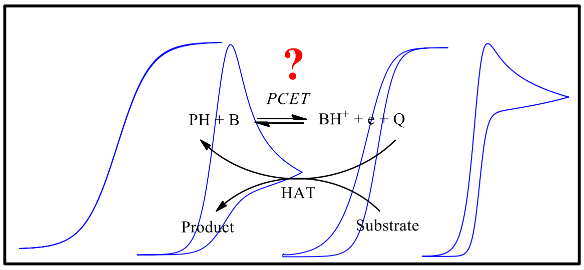
Proton Coupled Electron Transfer (PCET) catalysts will be presented in the framework of cyclic voltammetry (CV). Formal kinetic analysis of the various responses expected in the case of PCET catalyst following either stepwise or concerted pathways will be described. Both buffered solution and non-buffered aqueous media are considered. In the first case we show that, besides possible limitation by buffer diffusion, the PCET sequence may be rate limiting. CV wave shape, position and intensity are discussed in terms of thermodynamic and kinetic penalties associated to each mechanism. In the second case, we show that a non-classical *pseudo*-canonical cyclic voltammogram with hysteresis due to hydronium production is obtained for a Nernstian PCET catalyst with water as proton acceptor. Thermodynamic and kinetic penalties resulting from water based PCET specific pathways are analyzed. Then, we use this framework investigate the electrochemical catalysis of alcohol oxidation in water with a PCET catalyst, N-hydroxyphthalimide. We have found that the rate constant for benzyl alcohol oxidation is independent of *pH* strongly suggesting a true hydrogen atom transfer (HAT) as rate determining step. When water is the proton acceptor to generate the active form of the catalyst, i.e. N-oxyl PINO radical, the catalytic process follows a stepwise PTET pathway which kinetics partially limits the catalytic current.

Finally extension to heterogeneous PCET catalysts will be discussed with an application to an Oxygen Evolution catalyst.



All-in-one: removal of oxidizable (hydrocarbons) and reducible (sulfate) contaminants from contaminated groundwater in a single bioelectrochemical reactor

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Due to their high sustainability and low energy footprint, Microbial Electrochemical Systems (MES) represent promising candidates for in-situ remediation of contaminated groundwater. Still, only few studies have verified the capability of such systems to address complex mixtures of organic and inorganic contaminants so far.

This study concerned the performances of a lab-scale "bioelectric well" [1–3], a membrane-less tubular reactor containing a carbon-based anode (e.g., graphite, biochar) and a concentric stainless-steel mesh cathode, having the two electrodes hydraulically connected, yet physically separated by a polyethylene mesh. This system was tested for the treatment of "real" polluted groundwater obtained from a petrochemical site (Italy), containing a complex mixture of oxidizable (e.g., BTEX, PAHs, and other petroleum hydrocarbons) and reducible (e.g., sulfate, nitrate) contaminants. The "bioelectric well" was initially operated in fed-batch mode, and a potential of +0.2 V *vs*. SHE was imposed to the anode. After an initial acclimation phase, the system reached high oxidation rates of toluene (i.e., the main groundwater pollutant), with a Coulombic efficiency typically exceeding 90%. Interestingly, the molecular hydrogen generated at the cathode was then fully exploited for the biologically-driven reduction of sulfate. In a later stage, the reactor was also operated in continuous-flow mode by means of a peristaltic pump and its performance under pseudo steady-state conditions was thoroughly characterized.

Finally, the analysis of the microbiome composition and the quantification of key functional genes corroborated the chemical data and provided further insights into the performance of this novel bioremediation technology.

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Exotic Plasmonic Excitation of Electrons beyond The Normal Limit of Electrochemical Potential for Novel Photochemical Reactions

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Plasmon-powered processes to expand the ability of the spectroscopy regarding sensitivities in space, time, and energy resolutions. As their characteristics on localization of surface plasmons into molecule scale, huge intensity gradient of electromagnetic field would break the limit of light-matter interactions via the modification of the selection rule of the electronic excitation process. I have discussed about the possibility for the surface-enhanced-Raman scattering (SERS) as the probe to monitor the exotic electronic excitation processes [1]. Based on the observation of a small number of molecules at the plasmonic metal nanostructures by SERS [2-4], possibilities leading to the future innovative photo-functionalities were demonstrated by showing improved properties at optical manipulation of electrons and molecules, and ions [5-7]. We have shown that the localized surface plasmons of the Au nanodimer structures prepared on defect-free graphene provide highly-confined electromagnetic field to generate holes and electrons of the electrochemical potentials beyond the limit of far field light illumination [8]. Novel non-zero wavevector excitation results in the generation of highly reductive and oxidative powers for electrochemical reactions. Recent findings also prove the modification of electronic distribution of electrons under plasmonic excitation [9]. These findings provide a novel way to breaking the limit of photochemical reactions using various plasmonic materials.

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Electrochemiluminescence sensing and light generation confined in nanochannels

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Electrochemiluminescence (ECL) is light emission which triggered electrochemically in solution: reactive ECL species are generated by at electrode surfaces and undergo an electron-transfer reaction in solution generating the excited state of a luminophore, it subsequently returns to the ground state and emits a photon. ECL is widely and commercially used for biodetection, specifically in clinical immunosensing. Many diseases and other biomarkers can be detected by labelling antibodies with luminophores. The method several advantaged: sensing is background-free and allows straightforward highly sensitive detection in a very broad measuring range.

We employ nanofluidic electrochemical devices for light emission by ECL [1]. Microfabrication of nanochannels using photolithography, deposition and dry etching techniques allows the confinement of the reaction volume to a well-defined channel of 10 femtoliters. There, smallest quantities of luminophores participate in reactions. Nanoscale distances to electrodes enable very efficient reactions and bright light emission as well as novel reaction pathways.

The microfabricated nanochannel is connected to a bulk liquid reservoir via two small access holes. Thus, the reaction volume inside the channel can be geometrically decoupled from the reservoir, and the composition of reactants within the nanochannel, i.e., their oxidation states, depends on the potential applied to the electrodes embedded in the channel walls.

We demonstrate that, unique for ECL in nanochannels, reactions and light emission can be controlled by different biasing and reaction schemes to yield very distinct emission patterns. In particular, driving a annihilation electrochemiluminescence of tris(bispyridine)ruthenium(II) $Ru(bpy)_3^{2+}$ leads to constant light emission along the entire nanochannel, while a co-reactant pathway in which $Ru(bpy)_3^{2+}$ oxidation is triggered by tripropylamine limits light emission to nanochannel access holes [1].

Coreactant ECL reactions at the nanoscale could be employed for sensitive biosensing, e.g., ECL-labeled detection in immunoassays.

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Improving the Electron Transport of Single Molecular Junction with Redox-Active Center through Conjugated Chains

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Using single molecules to build a field-effect transistor is the critical step forward realizing future nanodevices with high efficiency and low energy consumption,[1-2] which has motivated a lot of researches over the world to achieve this ultimate goal. Redox-active molecules that could be converted between the oxidized or reduced states upon different electrochemical potentials, have been widely studied to illustrate the electrochemical gating at single molecular level. Their conductance could switch on as the energy levels of electrode shift to resonance with molecules. With this unique family of redox-active molecules, ongoing interest is to obtain a higher on/off ratio of conductance. However, achieving a high on/off ratio between the conductance of molecular junctions remains a great challenge and more factors of this single molecule system, like the molecular backbone, are needed to be explored.

Here a feasible strategy that connecting the redox-active moieties with conjugated chains was proposed to improve the electrochemical gating efficiency of molecular junctions using STM break junctions technique.[3-5] Benefiting from the low energy offset of frontier molecular orbitals, C=C-Fc-Py shows about one order larger maximum conductance enhancement and 160% improvement of conductance on/off ratio compared to C-C-Fc-Py at the equilibrium potential of Fc^+/Fc (**Figure** 1).

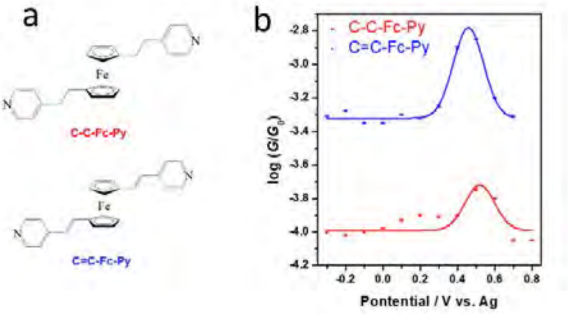

Figure 1. (a) Molecular structures of the investigated molecules. (b) The conductance of **C-C-Fc-Py** (red) and **C=C-Fc-Py** (blue) depends on the applied gate potential.

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Electrochemical synthesis of Ni/Al Layered Double Hydroxide and reduced Graphene Oxide composites for eco-friendly energy storage

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Layered double hydroxides (LDHs), also known as anionic clays, containing redox active transition metals are attractive compounds for electrochemical applications such as energy storage, sensors, fuel cells and catalysts for oxygen evolution reaction. [1] However, many LDH applications are still largely restricted due to their low electrical conductivity. Of course, this reduces the performances of electrochemical devices: in particular, supercapacitors need high currents flowing during fast charge−discharge cycles. These weak points can be overcome by combining LDHs with carbon nanomaterials, such as graphene. In the present work, we propose a one-step electrosynthetic protocol that produces nanostructured films of composites based on Ni/Al-LDH and reduced graphene oxide (GO).[2] This procedure contemporaneously allows for the LDH synthesis, the reduction of GO and its intercalation inside the layered structure. Up to date, the only interlayer anions introduced in LDHs coming from electrochemical syntheses are small molecules. This greatly constrains their applicability: in particular, our work could pave the way for further studies in the field of electrochemically induced intercalation chemistry. The films obtained have been thoroughly characterized by many techniques in order to verify the structure and morphology of the LDH/ERGO composites and to propose a theorization of the synthetic and growth mechanisms. Ultimately, we were able to employ these composites in the field of energy storage: the proposed hybrid super capacitor had a starting discharge specific capacity of 880 F g−1 which decreased and stabilized at 820 F g−1 after 300 cycles. The potential applicability of the device was also demonstrated by powering a red light-emitting diode. This work embraces the necessity of the development of systems with low environmental impact: in fact, we have proposed a binder-free device, safe, composed of hearth abundant element and able to work in aqueous electrolyte system with high performances. [3]

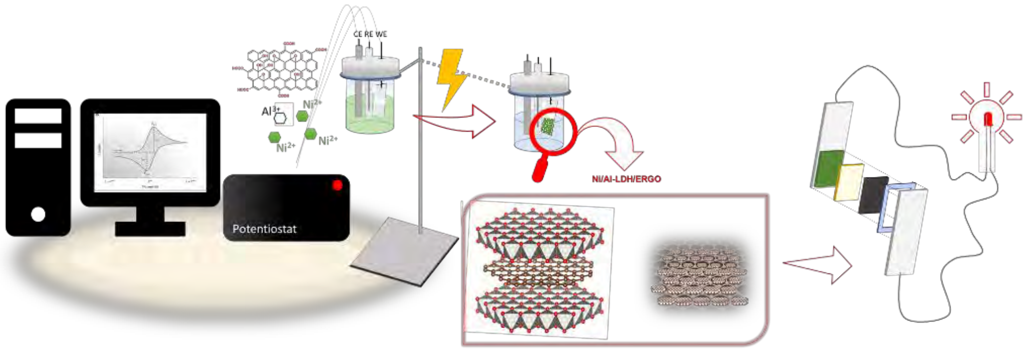

Figure 1: Sketch of the proposed work

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Cation-Disordered Materials with Pseudocapacitive Characteristics

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Cation-disordered Li_3VO_4 (LVO) has been identified as a promising negative electrode material for hybrid supercapacitors with theoretical specific capacity of 394 mAh g^{-1} (2 lithium accommodation) operating at a safe but still low potential range between 0.4 and 1.3 vs. Li/Li^+[1]. Recent our studies unveiled that cation-disordered LVO can be electrochemically obtained from the pristine cation-ordered LVO during initial cycling, which we termed as electrochemical activation process [1-2]. This electrochemical activation process induces the transformation of β-LVO from the pristine cation-ordered structure into an activated LVO, which has a Li^+/V^{5+} cation-disordered structure. Charge discharge curves also change from battery-like plateau to pseudocapacitive slope *via* such cation-disordering of LVO, along with its reaction mechanism change from two-phase to solid-solution reaction[2]. Yet, the preparation method of cation-disordered LVO has been a major issue as the electrochemical activation process is impractical from the industrial point of view. Such electrochemical process requires a precycling of β-LVO, which is difficult to control and inevitably produces undesirable irreversible capacity for a full cell assembling.

In this talk, we introduce two alternative processes to the electrochemical activation, *i.e.*, the direct synthesis of pseudocapacitive cation-disordered LVO materials (Figure 1). One is a simple mechanical milling of the pristine β-LVO powder, which brings about the full randomized Li^+/V^{5+} arrangement and thus enables to obtain thermodynamically metastable cation-disordered LVO phase without any precycling. Another is a partial substitution of V^{5+} with Si^{4+} in β-LVO, which results in a transformation of β-LVO into γ-$Li_{3+x}V_{1-x}Si_xO_4$. We present those two approaches, "fully" or "partially" cation-disordering, as new paths for transformation of battery-type materials into pseudocapacitive materials with improved electrochemical performances by simple cation mixing.

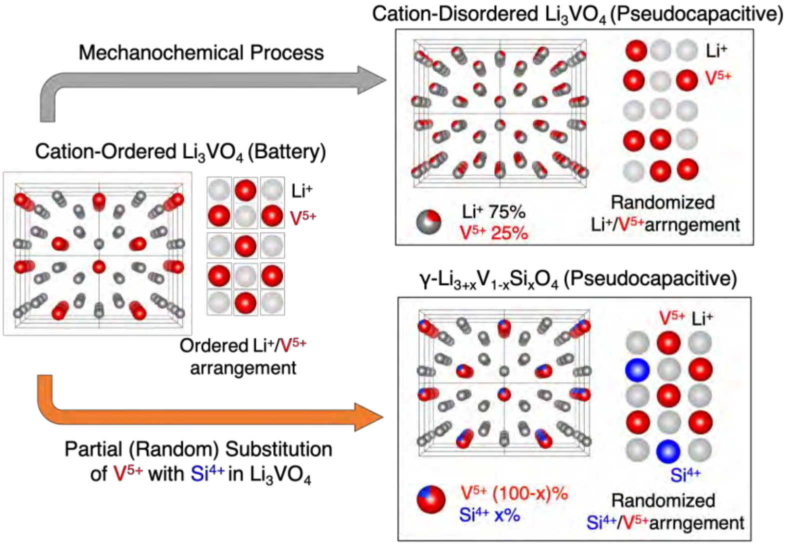

Figure 1. Schematic illustrations of two strategies for material transformation from "battery" into "psuedocapacitive" materials.

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Trace Metals Dramatically Boost Oxygen Electrocatalysis of N-doped Coal-derived Carbon for Zinc-air Battery

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The commercialization of metal-air batteries requires efficient, low-cost, and stable bifunctional electrocatalysts for reversible electrocatalysis of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). The modification of natural coal by heteroatoms such as N and S, or metal oxide species, has been demonstrated to form very promising electrocatalysts for the ORR and OER. However, it remains elusive and underexplored on how the impurity elements in coal may impact the electrocatalytic properties of coal-derived catalysts. Herein, we explore the influence of the presence of various trace metals that are notable impurities in coal, including Al, Si, Ca, K, Fe, Mg, Co, Mn, Ni, and Cu, on the electrochemical performance of the prepared catalysts. The constructed Zn-air batteries are further shown to be able to power green LED lights for more than 80 h. The charge-discharge polarization curves exhibited excellent and durable rechargeability over 500 (ca. 84 h) continuous cycles. The promotional effect of the trace elements is believed to accrue from a combination of electronic structure modification of the active sites, enhancement of the active site density, and formation of a conductive 3-dimensional hierarchical network of carbon nanotubes.

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Nanostructured mixed transition metal spinel oxide thin films as efficient electrocatalysts – composition, structure and properties

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Transition metal oxides have received renewed attention with their demonstrated usefulness as cathodes in dye-sensitized solar cells and as anodes in fuel cell [1, 2]. In addition, careful choice of the synthesis method and experimental conditions allow for the tailoring of the film nanostructure and surface area. However, it is clear from the literature [3,4] and our own work [5,6] that the experimental parameters used for the material preparation can greatly affect its electrocatalytic properties making it difficult to compare material performances. We have prepared various spinel oxides, namely $Cu_xCo_{3-x}O_4$ ($0 \le x \le 1$), $Ni_{1-x}Cu_xCo_2O_4$ ($0 \le x \le 0.75$), $Fe_yCu_{x-y}Co_{3-x}O_4$ and $Fe_yNi_{x-y}Co_{3-x}O_4$ (for y = 0.1 or 0.15 and x = 1 or 0.5 for both Fe-Cu and Fe-Ni containing oxides), using the thermal decomposition method. The films were analyzed, using several structural, chemical and electrochemical methods such as x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), cyclic voltammetry and X-ray photoelectron spectroscopy (XPS). The oxygen evolution reaction and electroreduction of hydrogen peroxide reaction were used as model reactions to determine the electrocatalytic activity of the electrodes.

The SEM analysis shows that the prepared thin films are quite porous and uniform. EDX analysis shows that a good correlation exists between stoichiometric and the resulting composition of the films. The formation of the spinel structure is confirmed by XRD analysis. For all our samples, the X-ray data also support the existence of the spinel structure. The addition of Cu to Co_3O_4 to form $Cu_xCo_{3-x}O_4$ resulted in an increase in roughness for x values from 0.25 to 1. When Ni is added to form the ternary oxides, the roughness more than doubles. For spinel oxides containing iron, nickel and cobalt, the roughness is much lower, i.e., around 80. Electrodes prepared by thermal decomposition method exhibit overall good catalytic activity towards oxygen evolution reaction and electroreduction of hydrogen peroxide. X-ray Photoelectron Spectroscopy (XPS), which probes the surface of the catalyst, was also used to understand the structure, composition and oxidation state of the metal ions in the ternary oxide materials. The high-resolution spectra for the Co, Cu and Ni 2p peaks indicate the existence of different Co^{2+}/Co^{3+}, Cu^{+}/Cu^{2+} and Ni^{2+}/Ni^{3+} ratio for these materials (the Fe signal was often too small in the XPS spectra to yield meaningful results). The analysis of O 1s spectra indicates that the main peak is composed of three components that can be assigned to lattice oxygen, adsorbed oxygen containing species such as hydroxides and surface bonded water. A detailed quantitative analysis will be provided in our presentation.

Electrochemical measurements show that for our samples, adding Cu to Co_3O_4 to form $Cu_xCo_{3-x}O_4$ and Ni to $CuCo_2O_4$ to form $Ni_{1-x}Cu_xCo_2O_4$ does not increase the material's electrocatalytic activity towards the oxygen evolution reaction, when the current is corrected for the real surface area. However, compared to Co_3O_4, our $Fe_{0.15}Ni_{0.35}Co_{2.5}O_4$, and $Fe_{0.1}Ni_{0.9}Co_2O_4$ ternary spinel oxides show significant enhancement with almost double the current density for the oxygen evolution reaction at 1 V under the same conditions. Our results will be compared with the morphology, structure, surface and bulk compositions, and electrochemical properties of spinel oxides films of similar compositions reported in the literature.

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Enhanced of ethylene glycol electrooxidation by hybrid catalytic systems

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Several types of fuels can be used in biofuel cells (BFCs) to generate clean energy. However, the low power density obtained is one of the main problems that limits the application of enzymatic biofuel cells. One strategy to improve power density of BFC is to increase the degree of oxidation of the fuel, so a higher number of electrons can be harvested [1]. Hybrid system combines the advantages of metallic or small molecular catalysts with biological catalysts (enzymes) in order to provide a gain in terms of the energy withdrawn from the biofuel and generate electricity [2]. We will discuss two different hybrids systems for the electrooxidation of ethylene glycol. The first system combines metallic nanoparticles of PtSn deposited on multi-walled nanotubes functionalized with COOH (MWCNTs-PtSn) and the oxalate oxidase enzyme (OxOx). The second hybrid system investigated combines an organic catalyst (4-amino-TEMPO (TEMPO-NH_2)) and OxOx. Both catalysts (MWCNTs-PtSn and Amino-TEMPO) showed electrochemical activity towards ethylene glycol oxidation presenting a well-defined oxidation peak. However, the onset potential for the inorganic catalyst is shifted 200 mV towards less positive potentials compared with the TEMPO one, making MWCNTs-PtSn more advantageous for power generation applications. Addition of the enzyme OxOx enhance the current densities observed. Inorganic hybrid system (OxOx+MWCNTs-PtSn) double the current peak in the presence of the enzyme. Amino-TEMPO/OxOx the enzyme acts only when the concentration of EG is higher than 100 mmol L^{-1}. Comparison of both approaches shows that OxOx+MWCNTs-PtSn is 10 times more efficient that the homogenous organic catalyst furnishing a good prototype to produce energy devices. The chronoamperometric experiments also confirms the good active of the hybrid systems; both MWCNT-PtSn-OxOx and amino-TEMPO-OxOx presented an enhancement of ethylene glycol oxidation, 34 % and 23 %, respectively, compared with the system in the absence of enzyme. Product analysis by *HPLC* confirmed the multiples catabolic steps of EG oxidation, enabling the oxidation of EG to more oxidable compounds when the hybrid system is applied. Overall, this study illustrates the development of an enzymatic biofuel cell using hybrid systems combining either an organic catalyst or metallic nanoparticles and enzymes in order to obtain a novel hybrid anode architecture to ethylene glycol oxidation. It constitutes a simple methodology with useful application in the development of enzymatic biofuel cells.

Keywords: Energy, Ethylene glycol, Oxalate oxidase, Inorganic catalyst, Organic catalyst, Enzymatic biofuel cell.

Acknoledgements: Fapesp (2014-50945-4; 2017-20431-7) and CAPES (001).

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Unconventional Electrochemical Precursor Stacks, Zn/Sn/Cu & Zn/Cu/Sn, for the Synthesis of CZTS

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Electrochemical stacked elemental layer (SEL) approach is one of the most exploited routes for the synthesis of Cu_2ZnSnS_4 (CZTS) [1]. This methodology typically involves the sequential deposition of the metallic layer followed by reactive annealing in a sulfur atmosphere. However, due to the limitations of aqueous chemistry, in the framework of electrodeposition the SEL approach has almost exclusively relied on the Cu/Sn/Zn sequence so far [1]. The zinc layer readily reacts upon the immersion in a copper/tin-based solution due to the difference between its reduction potential and that of the metallic dissolved ions. On the other hand, almost no limitations were observed for vacuum-based processes allowing to exploit different stacking order combinations [2], showing advantages with respect to the conventional one, such as the lower Zn and Sn loss after the high-temperature annealing. Therefore, the development of a suitable electrodeposition bath can bridge the technological gap between vacuum based and wet fabrication route in terms of possible stack sequences.

In our work, we investigated organic solutions based on ethylene glycol to overcome the intrinsic limitation of aqueous system [3] by reducing the reactivity between zinc and copper/tin ions in the solution. Displacement reactions are studied as a function of diethanolamine content in the bath, a suitable complexing agent for copper/tin ions. The solutions are characterized by cyclic voltammetry (CV), electrospray mass spectrometry (ESI) and, eventually, nuclear magnetic resonance spectroscopy (NMR). Zn/Sn/Cu and Zn/Cu/Sn stacks were fabricated by galvanostatic deposition and were characterized by scanning electron microscopy (SEM), electron dispersive spectroscopy (EDX), glow-discharge optical emission spectroscopy (GDOES) and X-ray diffraction (XRD). The copper-poor zinc-rich precursors obtained, were annealed in a sulfur atmosphere at 560 °C to obtain the CZTS, analyzed by Raman spectroscopy.

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Biofilm electrodes – can we push the limits?

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Biofilm electrodes are the living heart of the great majority of bioelectrochemical systems. Despite the recent progress, the further increase of the biofilm electrode performance is still a key issue for the future success of the deriving microbial electrochemical technologies. The current density of high-performing anodic microbial biofilms at flat, macroscopically smooth, electrode surfaces (e.g., at smooth polycrystalline graphite) reaches about 1 mA cm-^{2}, a further increase appearing hampered. Is this final limit in the performance of biofilm electrodes? Different approaches have been proposed to increase the electrode performance. They reach from surface structuring on a nanometer scale to a wealth of 3D electrode structures. How effective are such approaches? This presentation shows a systematic approach to the role of structural electrode dimensions on the short-term and long-term performance of biofilm electrodes. It also discusses opportunities by using promoting effects of unusual electrode materials, such as copper.

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Beuth L., Pfeiffer C.P., Schröder U. Copper-bottomed: electrochemically active bacteria exploit conductive sulphide networks for enhanced electrogeneity - submitted

Continuous separation of ionic contaminants and particles from water by shock electrodialysis

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Abstract: Shock electrodialysis (or shock ED) is an emerging technology for water purification and separations based on splitting fluid streams on either side of a deionization shock wave propagating through a charged porous medium at overlimiting current. This talk will introduce the basic physics and design principles of shock ED and will demonstrate possible applications in water remediation. When the feed is dilute, shock ED can be used for deionization (>99%) with high (85%) water recovery, which we demonstrated by removing ions of cobalt and cesium from model radioactive water. We also observed high (>90x) selectivity for multivalent ions by the continuous removal of magnesium (Mg^{2+}) from a dilute solution of sodium chloride as well as from artificial seawater. Selectivity for toxic heavy metals (which are often multivalent) at low salinity guarantees an ultra-low cost of electrical energy (~\$0.01/m^3 feed), which could lead to a practical solution to purify drinking water from corroded pipes or contaminated sources. In addition to ionic separations, this talk will also explore exotic separations such as removal of biological contaminants (disinfection) and nanoparticles (dielectrophoresis).

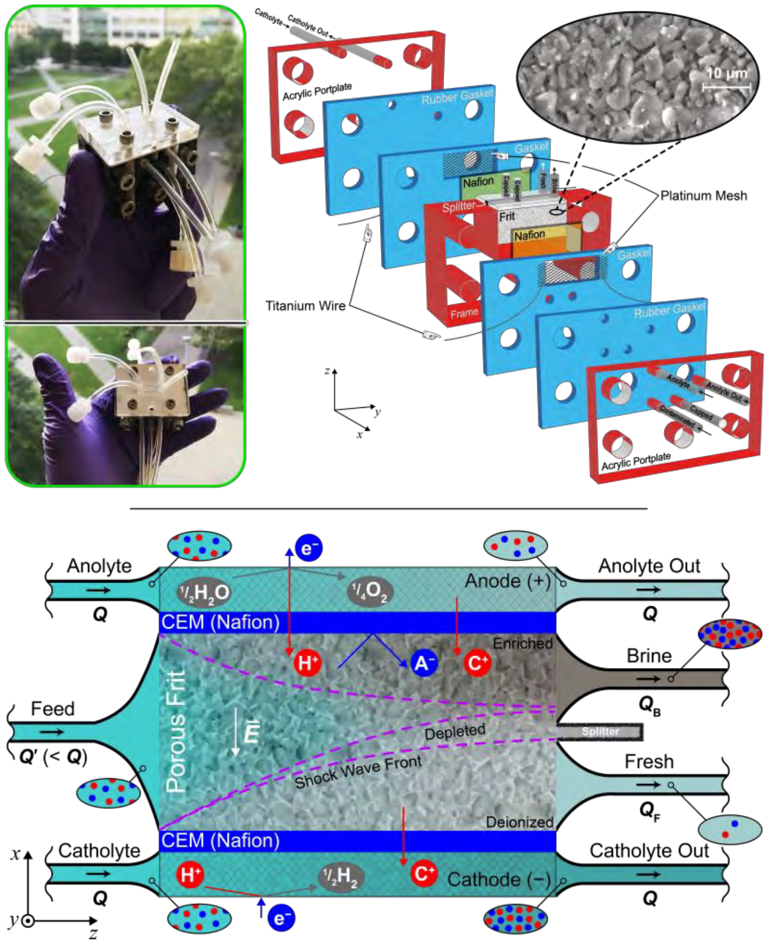

Figure 1: (top) Photographs and 3D illustration of the shock ED device to show assembly. (bottom) Rectangular cross section of the shock ED device to demonstrate the operating principles. For more details, please refer to Alkhadra et al., *Environ. Sci. Technol.* **2020**, *54* (1), 527–536.

Fingerprint of Fe-N-C Catalysts Poisoning for ORR Application in Microbial Fuel Cells

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The platinum-group metal-free catalysts (PGM-free) are the most performing and most affordable alternative solution to platinum catalyst into fuel cells. These catalysts are carbonaceous materials containing central atomic transition metals like Fe, Co, Mn coordinated to nitrogen bonded into the carbon matrix. The metal-nitrogen-carbon (M-N_x-C) in which the nitrogen coordination is 2, 3, 4 nitrogen is the most desired active site [1] to enhance oxygen reduction reaction (ORR) kinetics at all pH values [2,3]. Despite the intrinsic difference in active sites between PGM and PGM-free catalysts, PGM-free are able to deliver very satisfactory current density especially in a contaminated working environment where Pt is easily deactivated. This is particularly beneficial in Microbial Fuel Cells (MFC) application field, where wastewater can be exploited as a new source of energy. The Fe-N_x-C coordination ability to withstand very harmful contaminants has been studied in detail to identify the fingerprint of coordination contamination in the case of typical wastewater contaminants, namely nitrite, nitrate, chloride, perchlorate, sulfide, and sulfate. Rotating Disk Electrode (RDE) analysis, Koutecky-Levich analysis, and Tafel analysis have been exploited to identify specific trends at pH 7 in terms of Onset Potential (E_{on}), Halfwave potential ($E_{1/2}$), Limiting Current Density (J_{lim}), Number of Transferred Electrons (#e^-), Tafel slopes, and exchange current density (J_0) at the variation of contaminants concentration. The results showed a very peculiar trend in the case of direct active site poisoning with J_0 as the predominantly parameter able to exactly distinguish between specific and unspecific bonded contaminants.

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The Electric Double Layer in Carbon Nanotubes and -slits

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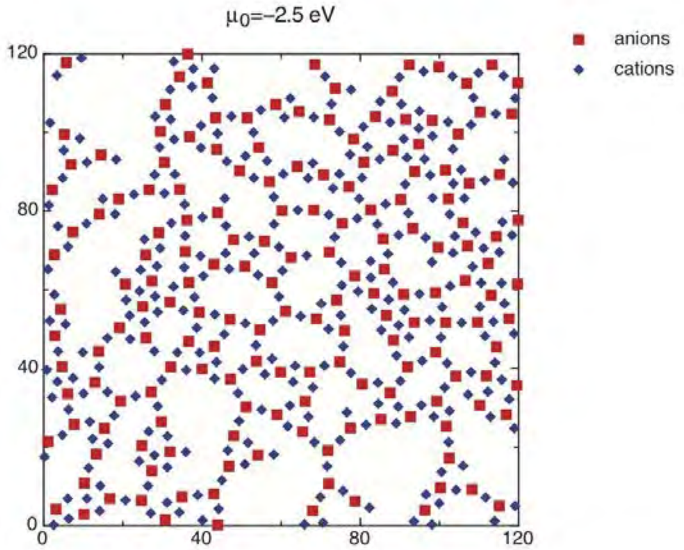
The diameters of nanotubes and nanopores can be much smaller than the Debey lengths of electrolyte solutions. In this case, conventional double-layer theory cannot be applied. In order to understand the behavior of electrolytes under such conditions, we explore the interactions between ions, molecules, and carbon nanostructures such as graphene and nanotubes. Because of the low density of electronic states the adsorption or insertion of ions modifies the electronic properties of the carbon structures. In particular, they make semiconducting nanotubes locally conducting, converting them into degenerate n- or p-type semiconductors.

In contrast, the interaction of water with carbon structures is weak. In the case of narrow nanotubes, the image charge on the walls of the tube weakens the solvation of ions with water. Also, the presence of water hardly affects the interaction of ions across the walls of a nanotube.

On the basis of the elementary interaction of ions with carbon materials we have performed Monte Carlo simulations for an ensemble of ions inside a carbon nanoslit in the grand-canonical ensemble. Two regimes can be distinguished: A gas-like filling of the slit with a low density of ions, and a disordered, glass-like structure at high ionic concentrations. The two regimes are separated by a transition region reminiscent of a phase transition, in which transient, string-like structures are formed – see figure. Both the charge and the electrochemical potential are well defined in these ensembles. This allows us to calculate capacity curves without introducing adjustable parameters. The structure of these curves, in particular the number of capacity humps, depends on the details such as the hydrophilicity of the slit, and the charge number of the ions. A few typical examples will be presented.



Transient structures at the transition between a gas-like and a solid-like 2D ensemble of ions.

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Influence of electrolyte selection on anodic memristors behavior

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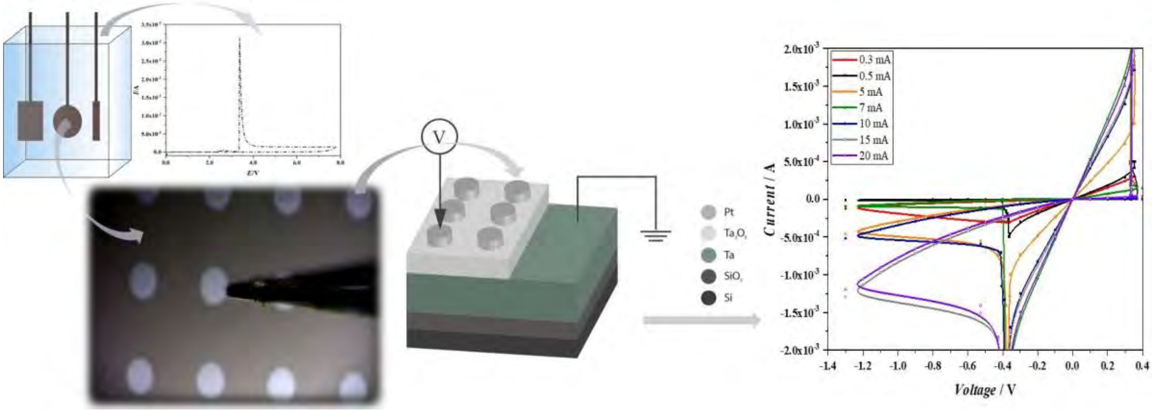
As a borderline case amongst electroactive processes, the electrical field activated charge transport through a solid state material is responsible for the switching of a memristor between its different electrical conductivity states. These have a permanent character, thus the term of memory-resistor shortened as memristor is widely used. Among various materials, Ta oxide memristors play a very important role in the next-generation of thin film micro- and nano-electronic devices mainly due to applications in non-volatile redox-based resistive switching memories (ReRAMs) and artificial neural networks. Thus, there is a strongly motivated research interest for understanding the mechanism of device operation based on the electric field assisted formation of conductive filaments inside an insulating metal oxide layer. Due to its valve metal characteristics, anodic oxide formation on Ta is a reliable, controllable, reproducible, cost-efficient and industrially implementable approach for memristor fabrication. Such anodic oxide, also regarded as a solid electrolyte, is interposed between the Ta parent metal and a Pt thin film top electrode for defining a memristive device.



In this work, metal-insulator-metal (MIM) structures defined using thin and ultra-thin films of $Pt/Ta_2O_5/Ta$ were investigated in order to study ion migration during filament formation. Using sputtering, 330 nm thick Ta films were deposited on SiO_2/Si wafers. The metallic films were anodized potentiodynamically up to 20 nm thickness in three different electrolytes: phosphate buffer (PB) citrate buffer (CB) and borate buffer (BB) solutions with different rates of potential increase. Before electrical characterization, Pt top electrodes 200 µm in diameters were patterned on top of the oxide layer. The nature of anodic oxide was questioned from the point of view of anodization parameters. Electrolyte species may get trapped inside the memristive device due to anodization conditions and they can directly affect the filament formation during the memristive switching. Different compliance currents (I_{cc}) were studied during the memristor formation phase and their effects on final device properties are reported. The obtained memristors have shown very good switching properties, e.g. ability of long endurance, long retention ($>10^5$ cycles, $>10^6$ cycles with $I_{cc} < 150$ mA), low power consumption ($V_{set}/V_{reset} < \pm1.5$ V) and multiple switching levels. Thermo – electrical measurements were also performed resulting in reliable memristor formation dependence on the applied compliance current. The figure shows anodization process of Ta film with the schematic representation of the memristive devices and their *I-V* response.

In conclusion, the current study offers optimized routes for fabrication of anodic Ta oxide memristive devices offering possibilities for future sensing applications and large scale-up opportunities with the main advantage of a very simple and cheap fabrication procedure.

Electrochemical nitrite sensor based on PEDOT and hollow AuPt nanoparticles

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Nitrites are chemical compounds that can pose a threat to the environment and human health at concentrations above 3 mg/L in drinking and waste water (World Health Organization [1]). These compounds can react with amines and form N – nitroso compounds, some of which are potentially carcinogenic products, and can lead to cyanosis through the formation of methemoglobin by the reaction of nitrites and hemoglobin. Therefore, monitoring the concentration of nitrite in water is an essential task.

Traditionally, nitrite ions are detected and quantified by techniques that require complex devices, are time consuming or demand the pretreatment of the sample with some harmful reagents or the production of toxic compounds. These detection methods encompass colorimetry, chemiluminescence and chromatographic and spectrophotometric techniques.

Electrochemical sensors are an appropriate alternative for the detection of nitrite in water. Nanocomposites based on multiwall carbon nanotubes, graphene, conducting polymers and metal nanoparticles have been reported as nitrite sensors [2,3]; however, to the authors´ best knowledge, sensors based on PEDOT and hollow bimetallic nanoparticles have not been tested as potential materials for the electrochemical detection of nitrite.

In this work, hollow AuPt nanoparticles were synthesized by galvanic displacement and characterized by SEM, EDX and TEM/STEM. The results confirmed the hollow structure of the bimetallic nanoparticles (particle size: 20 -30 nm; Fig 1). EDX analysis revealed that the particles contain Au and Pt and showed the elemental profile through the nanoparticles. The nanoparticles were centrifuged, resuspended in water and co-deposited from a solution of the surfactant SDS, the monomer EDOT and $LiClO_4$ at 0.9 V. The performance of the composite PEDOT/AuPt was evaluated by differential pulse voltammetry (Fig. 2) in the range of 50 to 250 µM. The sensitivity of the sensor was 0.04 +/-0.01 µA µM^{-1}.

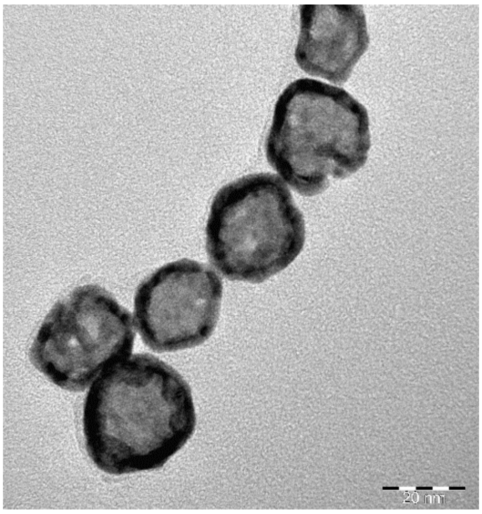

Figure 1 – Hollow AuPt TEM micrograph

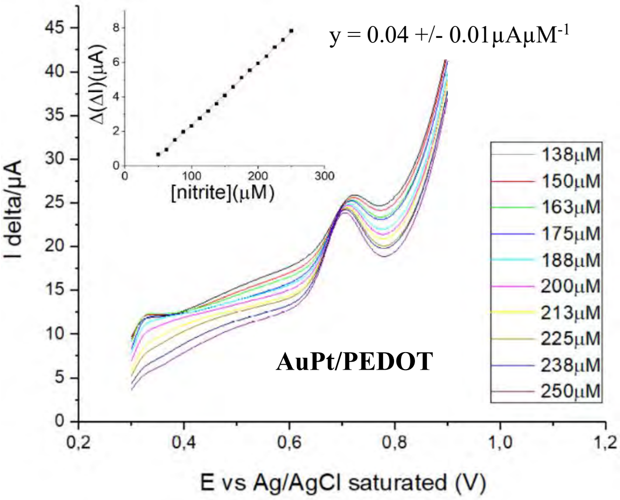

Figure 2 – DPV curves for nitrite detection

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Nernstian Li^+ Intercalation into Few-Layer Graphene and its Use for the Determination of K^+ Co-Intercalation Processes

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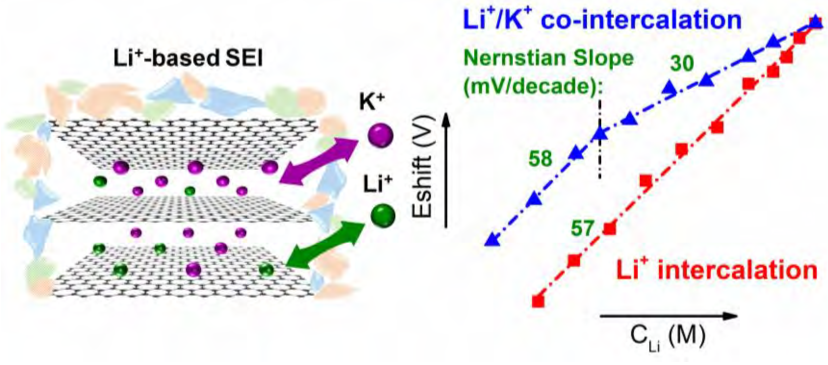
Alkali ion batteries (AIB) based on Li^+, and emerging technologies based on K^+, are important high-performance rechargeable energy storage devices. Alkali ion intercalation is fundamental to those battery technologies for a wide spectrum of potential applications that permeate our modern lifestyle, including portable electronics, electric vehicles, and the electric grid. In spite of its importance, the Nernstian nature of the charge transfer process describing lithiation of carbon has not been described previously.

Here we use the ultrathin few-layer graphene (FLG) with micron-sized grains as a powerful platform for exploring intercalation and co-intercalation mechanisms of alkali ions with high versatility. Using voltammetric and chronoamperometric methods and bolstered by density functional theory (DFT) calculations, we show the kinetically facile co-intercalation of Li^+ and K^+ within an ultrathin FLG electrode. Furthermore, distinct Nernstian-type responses for Li^+ only and Li^+/K^+ co-exist systems with respect to solution concentration were observed, with the previous one showing a single Li^+ charge transfer property upon (de)intercalation and the latter one showing a two-phase Li^+/K^+ co-intercalation behavior. Bulk ion diffusion coefficients in the carbon host, as measured using the potentiometric intermittent titration technique (PITT) were similarly sensitive to solution composition. While previous studies of co-intercalation on graphitic anode typically focus on co-intercalation of solvents and one particular alkali ion, this is to the best of our knowledge the first study elucidating the intercalation behavior of two monovalent alkali ions. This study demonstrates the concept of alkali ion co-intercalation for elucidating fundamental charge transfer processes for batteries *beyond Li-ion*, and establishes ultrathin graphitic electrodes as an enabling electroanalytical platform to uncover thermodynamic and kinetic processes with high versatility.



Spatially resolved model of oxygen reduction reaction in porous gas-diffusion electrodes

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Chlorine is one of the most important basic chemicals, which is predominantly manufactured by the energy-intensive chlor-alkali electrolysis process. By introducing the so-called oxygen depolarized cathode (ODC), the electrical energy demand can be reduced by up to 30 % compared to the state-of-the-art membrane process. The ODC is designed as a gas diffusion electrode (GDE), due to the low solubility of oxygen at the high process temperature (80 °C). To improve the efficiency of GDE further it is necessary to understand the complex interaction of transport and reaction processes inside the electrodes.
In order to investigate these processes a stationary mathematical model is developed, which includes the physical transport processes inside the gas and liquid phase as well as phase transformation and electrochemical reaction kinetics at the three-phase boundary (Fig. 1, left).

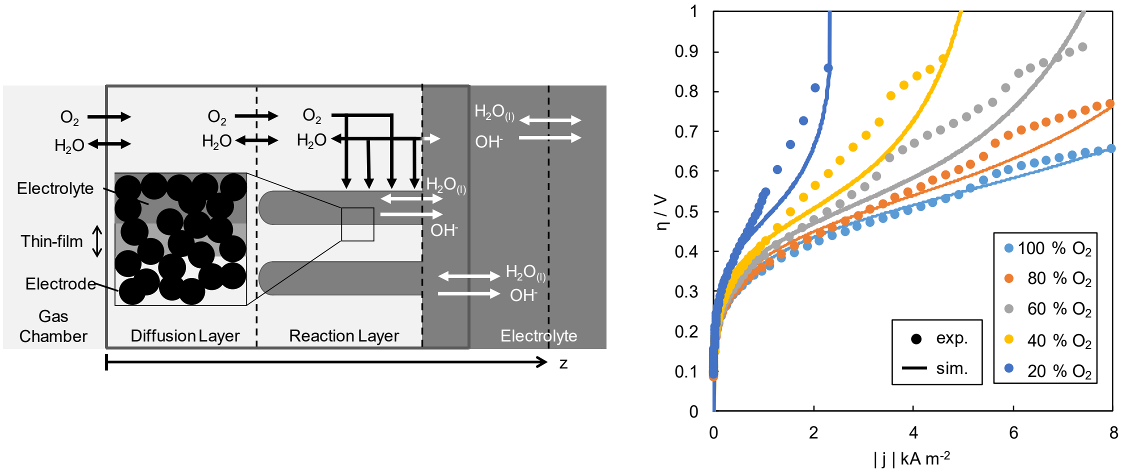

Fig. 1: Left: Schematic of the approach according to the TFFA model. Right: Measured and simulated polarization curves (80 °C, 30 wt.% NaOH) for different oxygen concentrations.

In contrast to earlier assumptions [1], recent findings by Botz et al. [2] showed the importance of the electrolyte transport inside the GDE which was underestimated in the current thin-film flooded-agglomerate (TFFA) models. In the improved version of the TFFA model, the electrolyte transport is considered adequately. The electrolyte properties inside the GDE and the resulting process parameters, such as the oxygen solubility, are spatially resolved, allowing a detailed glimpse into the physical and electrochemical processes inside the GDE.
The model is validated by a custom build test setup designed for stationary conditions. A large circulating electrolyte system, accurate gas dosing, as well as individual pressure and temperature control for the electrolyte and gas phase guarantee stationary conditions for long-term measurements. A wide range of process conditions can be adjusted and used for model validation. The results show a good agreement between measured and simulated overvoltages for different oxygen concentrations (Fig. 1, right).

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Novel Non-precious Metal Nanocomposites as Potential Cathodic Electrocatalysts for Microbial Electrolysis Cells

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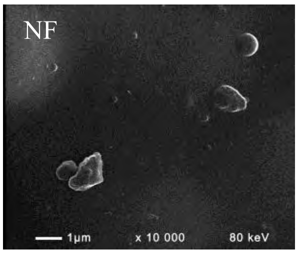
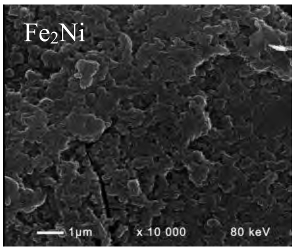
Microbial electrolysis cell (MEC) is an emerging bioelectrochemical technology for hydrogen production from wastewater and other renewable resources, which major advantage is the relatively low voltage input (0.2–0.8 V) compared to the conventional water electrolysis (1.23–1.8 V). Because MECs use the same bioanodes as microbial fuel cells, the most critical challenge for their practical application is the development of cost-effective cathodes for near-neutral pH and ambient temperature conditions.

In this study, two- and three-component nanostructures, denoted as Fe_2Ni, Fe_3Ni Fe_2Co, Fe_3Co, CoNi, $CoNiFe_2$, and $CoNiFe_3$, were deposited on nickel foam (NF) by a new method called "Dip and Drying" (DDM) [1,2]. The DDM allows a fast self-deposition of nanoparticles upon the metal substrate at room temperature. The deposition was performed from mixed 0.1M solutions of $FeCl_2$, $FeCl_3$, $CoCl_2$ and $NiCl_2$, in different combinations for 30 minutes. The morphology and the chemical composition of the developed materials were analyzed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The electrocatalytic activity of the modified electrodes for the hydrogen evolution reaction (HER) in neutral phosphate buffer solution (PBS) was explored by linear sweep voltammetry (LSV), cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The results obtained show that the nanocomposites, deposited from Fe^{2+} solutions, possess higher electrocatalytic activity than those from Fe^{3+}-containing electrolytes. The highest hydrogen production rate of 38±2 $ml.cm^{-2}.min^{-1}$ at -1.2 V (vs. Ag/AgCl) was achieved with Fe_2Co-NF electrode. Further studies, aiming at the practical application of this type of electrodes as cathodes in MECs, are going to be performed.





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Intelligent Microelectrodes Arrays for *In Situ* Analysis of Biofluids

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Electrochemical lab-on-a-chips (LoCs) are translational and mobile analytical micro-systems that enable rapid and label-free analyses of redox biomarkers, bringing benchtop medical diagnostic methods to the point-of-care. However, the selectivity of these LoCs towards the biomarkers-of-interest dramatically decreases in the presence of biofluids due to other redox molecules generating masking and overlapping electrochemical signals, requiring pretreatment steps to filter the interfering molecules and limiting the LoC's real-time analysis capabilities. Here we report a new electroanalytical technique that will enable biofluids analysis without pretreatment step and lies in the use of an array of microelectrodes that are modified by coating with bioelectronic films and generating a set of complex electrochemical signals that is analyzed by using intelligent machine learning algorithms (chemometrics) (Fig. 1A). We utilize electrodeposition method [1,2] to modify electrodes with bioelectronic nano-films (e.g., reduced-graphene-oxide and biopolymer chitosan). The modified array controls the electrochemical signal characteristics based on the diffusion and electron transfer rate coefficients of the redox molecules. We analyze biofluids in two detection modes: (1) direct detection of a specific biomarker and (2) simultaneous detection of multiple biomarkers by using machine learning algorithms. We demonstrate the proof-of-concept detection of: (1) amplifying antipsychotic clozapine electrochemical signal by using the reduced-graphene-oxide film that enables *in situ* detection in 20 µL of whole blood (within 5 minutes; limit of detection of 0.64 ± 0.04 µM, which is better than the clinical threshold) and will provide better schizophrenia treatment outcomes (Fig. 1B); and (2) utilizing an array of microelectrodes modified with various selectivities (chitosan and chitosan-carbon nanotubes) to different neurotransmitters and analyzing the set of signals generated from profiles of neurotransmitters by using a machine learning algorithm (artificial neural network and partial least square regression) enables their simultaneous differentiation (dopamine limit of detection of 9.3 mM and norepinephrine limit of detection of 6.7 mM) in undiluted urine (Fig. 1C).

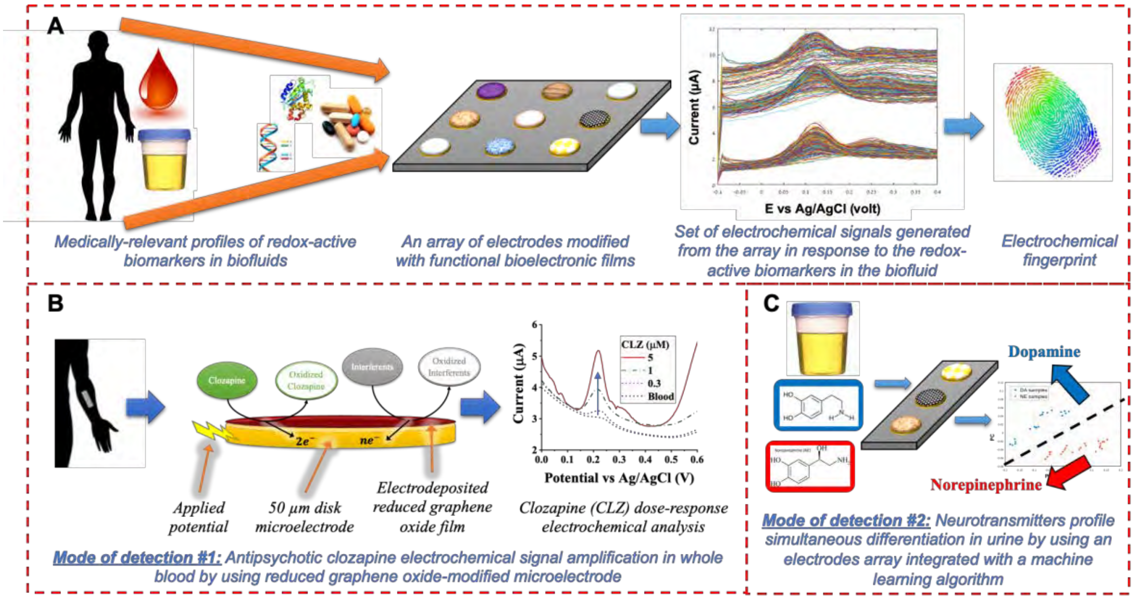

Figure 1: (A) Electrochemical lab-on-a-chip integrated with functional bioelectronic films for real-time and *in situ* probing of redox biomarkers in biofluids. (B) Amplification of antipsychotic clozapine electrochemical signal. (C) Intelligent electrodes array for neurotransmitters profiling.

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Electrochemical and spectroscopic properties of Green Synthesized Gold Nanoparticles Doped in Polyacrylonitrile Nanofibers

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Abstract

The paper provides insights on the less costly and eco-friendly green technique used for the synthesis of gold metal nanoparticle from banana (Musa paradisiaca) peel extracts. Electrospinning method was used to fabricate a stabilized nanocomposite polyacrylonitrile functionalized with green synthesized gold (PAN/Au) into nanofibers. The nanoparticle and its nanocomposite were characterized by using spectroscopy and surface morphology techniques. Surface characterization techniques like transmission electron microscope (TEM) was used to determine the shape and size of the nanoparticles. Other spectroscopy characterization was done by using UV-Visible spectroscopy, and X-ray diffraction (XRD), respectively. The spectroscopic studies for the gold nanoparticles were conducted at various volumes, concentrations, and synthesis time. The nanoparticle diameters were calculated to be on an average of 9 nm. Shape uniformity, stability and particle size distribution of the nanoparticles and nanocomposite were confirmed by TEM and Zeta Potential study. The electrochemical characterization of synthesized nanoparticles Au and its nanocomposite PAN/Au was carried out by using cyclic voltammetry (CV), Furthermore, the nanocomposites of gold nanoparticles doped in polyacrylonitrile nanofibers showed improved electrochemical information as compared to the monometallic nanoparticles, unmodified PAN molecule, and the bare glassy carbon electrode. These properties exhibited by the nanocomposite PAN-Au suggests that it can be used as electrochemical sensors for the detection of biological molecules such as neurotransmitters.

Preparation of Covalently Attached and Robust PANI Nanorod Arrays Using an Oriented Mesoporous Silica Film as Hard Template

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Polyaniline (PANI) is a thoroughly studied conducting polymer known for its structural diversities, high electrical conductivities, doping/de-doping and protonating/deprotonating chemistry, facile synthesis and environmental stability. Distinguishable among the family of conjugated polymers, it offers interest for numerous applications including sensors, energy harvesting and storage, memory devices, filtration membrane or anticorrosive coating.[1] For practical applications the structural design and fabrication at nanoscale (with controlled size and shape) is important for tuning their physical properties. Polyaniline nanostructures have been synthesized in different morphological shapes including nanofibers, nanorods and nanotubes, by using various synthetic methods such as template synthesis, emulsion, self-assembly and interfacial polymerization.[2] Aligned and ordered nanostructures are expected to exhibit better electrochemical and electronic properties than the randomly oriented nanoscale materials, as exemplified for polyaniline nanostructures showing high and reproducible performance as material of device.[3.]

One of the major issue is the PANI stability when deposited by drop-casting or electropolymerized over the surface. The lack of proper chemical bonds between the polymer chains and the conducting substrate, limits the practical applicability of PANI regardless of its excellent chemistry. It is thus necessary to get stable and covalently bonded PANI nanostructures.

In this work, PANI nanowires have been electropolymerized on ITO substrate covered with a mesoporous silica membrane and containing aniline molecules covalently attached at the bottom of the pores. The oriented mesoporous silica thin film was generated on ITO by electrochemically assisted self-assembly.[4] The ITO surface was first derivatized with aminophenyl molecules by in situ electrografting, according to a reported procedure,[5] followed by potentiostatic polymerization of PANI (for selected times) from a bath containing aniline in sulfuric acid media [6].

The electrografted arylamine molecules stabilize the PANI nanorods arrays and acts as catalysts during electropolymerization (see Fig. 1 indicating faster filling of mesochannels observed for the aniline-grafted sample, and mechanically stable deposits upon silica removal). The PANI nanowires exhibit excellent electrochemical redox behavior inside the silica pores and after removing the template. Its redox behavior was further studied by spectro-electrochemistry. Other physico-chemical methods including X-ray photoelectron spectroscopy, grazing-incidence small-angle X-ray scattering and transmission electron microscopy, were also used to characterize the materials.

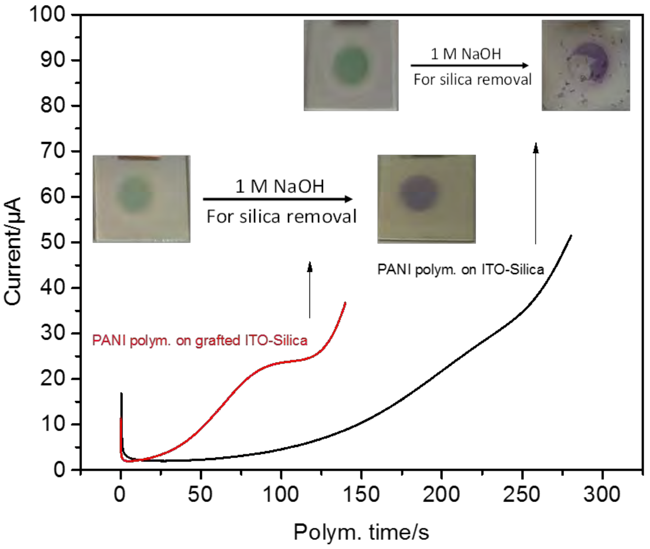

Fig.1. PANI polymerization steps on ITO-silica film and their relative stability after treatment with 1 M NaOH for silica template removal

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Combined Spectroelectrochemical and EQCM Study of Magnesium Porphine Electropolymerization Process

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Mg(II) porphine (MgP, Fig. 1_left) can be polymerized by its oxidation in acetonitrile (AN) solution. If the potential is sufficiently low (below 0.4 V vs. Ag/10 mM $AgNO_3$ in AN for potentiostatic deposition) an electroactive polymer film is steadily growing [1]. It is known that MgP oxidation under mild conditions should lead to single bond's formation in *meso-meso* positions. It implies that a porphine monomer unit may form from 2 to 4 such bonds inside the polymer.

Recently this process has been studied via both spectroelectrochemical [2], EQCM and redox-charge [3] methods in order to determine the average number of such bonds and consequently to establish the polymer structure.

The former technique monitors the variation of the UV-visible spectrum of the monomer solution in the course of its oxidative electrolysis, with separation of the monomer and solute oligomer contributions. It provides the relation between the electrolysis charge and the amount of the oxidized monomer. Their ratio reflects the charge consumption for formation of bonds inside the polymer and solute oligomers as well as for their transition to the oxidized (conducting) state.

Even though the latter contribution may be evaluated on the basis of the redox-charge variation of the deposited film in the monomer-free solution, one cannot find the number of bonds per monomer unit since a significant fraction of the oxidized monomer gives solute oligomers and polymer particles in solution or on the bottom of the cell.

Supplementary information for determination of the monomer fraction inside the polymer film on the electrode surface is available from the EQCM technique via measurements of the variation of the film's mass in the course of both its deposition and redox-charge variation in contact with background solution.

Data for all these three methods have been combined via the set of equations based on the mass and charge conservation laws.

Their solution has shown that the variation of the redox-charge of the film is accompanied by exchange with the background solution by not only counterions but also by solvent molecules, due to the film rigidity at this time scale. This analysis has confirmed a very high yield of the film deposition at the electrode surface: about 90% of all MgP monomers oxidized in the course of the oxidative electrolysis were transformed into monomer units inside the film. The average charging degree of the monomer unit inside the film at the deposition potential has turned out to be in agreement with our previous estimates, about 0.15. At last, the average number of the bonds between monomer units inside the film is around 2.3-2.4. It means that the polymer in general has got a chain structure (Fig. 1_right) but with a significant number of interchain links (around 3 to 4 links per 10 monomer units of the chain).

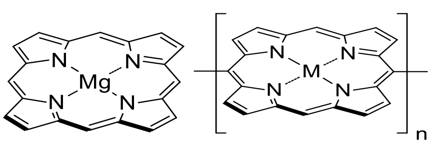

Fig. 1. Left: MgP monomer. Right: Mg(II) polyporphine deposited at very low oxidation potential, pMgP-I

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Copper nanowires as higly sensitivite electrode for nitrate ions in water

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Agricultural and livestock sectors are the main sources of nitrate ions contamination in water and foodstuff. [1]. High nitrate concentration is dangerous for both environment (algae overgrowth) and human health. Nitrate ions can be converted in different harmful nitrogen based compound such as NO_2^-, NO, N-nitroso compounds [2] that are responsible of several diseases such as cancer, Parkinson [3-4]. For these reasons, the Environmental Protection Agency, has established the maximum amount of nitrate ions in drinkable water at 44 mg/l, limit that is valid in many European countries [5]. Generally, spectroscopy techniques are the most used because allow to carry out analyses with high precision and reaching low LOD but it requires skilled workforces and specific instrumentations, besides the procedure is long and hard [6]. In this frame, electrochemical sensors can be used as easy, fast, cheap and not-lab-depended technology to detect nitrate ions with high selectivity and sensitivity. Copper is one of the more sensitive material to detect nitrate due to its low overpotential for reduction of NO_3^- to NO_2^- [7-9]. In this work, we have developed a Cu-NWs based electrode obtained by template galvanic deposition into nanoporous membrane. The overall process is cost effective, scalable, fast and Cu NWs of well anchored to a copper current collector can be easily obtained. Using this kind of nanostructured electrode, the surface area of the sensor is of about 70 time higher of bare ones and this is a special property for electrochemical devices. A low LOD of about 9.1 µM, (≈ 100 times lower than EPA limit) and a wide linear range were found. The effect of many interferents (Mg^{2+}, CO_3^{--}, Cu^{2+}, Pb^{2+}, Zn2+, Ni^{2+}, Hg^{2+}, Ag^{+}, Al^{3+}, SO_4^{--}, Na^{+}) was studied and nitrate ions were also successfully detected in real water samples (river, rain and drinking water).

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Ascorbic Acid detection using linear sweep voltammetry on flexible electrode based on gold nanoparticles and reduced graphene oxide

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In the last years, sensors are taking more and more relevance in many fields such us, sport [1], environmental [2], health [3]. In the food field sensors can help to maintain the quality index for example by measuring the freshness, the allergens and the content of the contaminants or to improve the food-status monitoring by minimizing the waste and increasing the shelf-life.

In this work, an electrochemical sensor for ascorbic acid determination is shown whit a real validation for its determination in milk.

Ascorbic acid (AA), also known as vitamin C, is a water-soluble compound with antioxidant properties. It can be found in nature in many fresh fruits and vegetables like oranges, potatoes and cauliflower [4]. Due to its antioxidant properties, it is widely used in the food industry. It may be added to many foods and beverage to improve keeping qualities and it can be also used as a color/flavor stabilizer. Moreover, AA can be employed as a browning inhibitor to increase antioxidant food capacity. It plays a fundamental role in many biological functions such as iron absorption, collagen synthesis, immune system activation, osteogenesis [5]. Most plants and animals synthesize ascorbic acid from carbohydrate precursors including glucose and galactose. Humans and other animals are unable to produce this vitamin and thus it is necessary to be taken from the diet [6]. A lack of AA can cause scurvy pathology that affects collagen synthesis. Ascorbic acid deficiency leads to symptoms of weakness, anaemia, gum disease and skin problems. An excess of AA leads to gastric irritation and renal problem. Moreover, it can react with the heavy metals as pro-oxidant, increasing the oxidative stress in human cells.

For all these reasons, it is important to evaluate ascorbic acid concentration in food and beverage. In this work indium tin oxide (ITO) coated on flexible polyethylene terephthalate (PET) substrate electrode was modified with reduced graphene oxide and gold nanoparticles by simple co-electrodeposition performed at room temperature. All samples were characterized by electron scan microscopy and EDS analysis. Because the AA oxidation highly depends on the pH of the sensing solution, a systematic investigation on the effect of this parameter was performed.

The as prepared electrode was used as electrochemical sensor to selective detection of ascorbic acid using linear sweep voltammetry. Promising results were obtained. In particular, a linear range from 20 to 150 µM of ascorbic acid and a limit of detection of about 3.1 µM was found. The sensors have a reproducibility of about 5.5% and also show high selectivity towards different milk interferents such as chlorine, calcium, magnesium, sulphate ions, sodium and glucose. Ascorbic acid was detected also in different commercial milk samples demonstrating the possibility to quantify this analyte in real samples with a very cheap method.

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Electro-chemo-mechanical coupling: a novel approach to micro actuation

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The chemo-mechanical effect in solids refers to dimensional change due to change in stoichiometry. Dimensional change due to electrochemically-induced compositional change has been termed the electro-chemo-mechanical (ECM) effect. The mechanical instability inherent in this effect is clearly deleterious for batteries or fuel cells, but, as recently suggested, has potential for use in actuation[1]. The structure of an actuator device that operates on the ECM principle comprises a micrometer thick solid electrolyte (SE) sandwiched between two ECM-active, working body (WB) layers. An electrochemical reaction must occur in these layers, causing them to alternately expand or contract. In order to facilitate the ECM response, the WB layers should have mixed ionic and electronic conductivity and a large chemical expansion coefficient.

We have constructed a 2mm diameter thin film membrane ECM actuator device comprising 20mol% Gd doped CeO_2 (20GDC) as the SE and [$TiO_{2-\delta}$\20GDC] composites as the WBs. Selected area electron diffraction measurements showed the composite to be nanocrystalline, a morphology that promotes interfacial oxygen ion diffusion. Synchrotron X-ray absorption measurements detected a mixture of Ce^{3+}/Ce^{4+} (~[0.4]/[0.6]) and Ti^{3+}/Ti^{4+} (~[0.1]/[0.9]) oxidation states in the WB. The deformation of the ECM actuator was observed to be in the bending regime producing large vertical displacements (~3 μm) and ~4 MPa stress. The stress/voltage ratio yields a pseudo piezoelectric stress coefficient of e_{31}=1.26 C/m^2, comparable to common lead free piezoelectrics such as lithium niobate, lithium tantalate and alkali niobates.

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Electrochemical synthesis of Prussian blue from iron impurities in 3D-printed graphene electrodes: Amperometric detection of H_2O_2

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Three-dimensional (3D) printing has been exponentially applied in chemistry with relevant applications in material science and electrochemistry. Fused deposition modelling is the most affordable 3D printing technique and thus has been widely used for the fabrication of electrodes for energy storage and sensors. Commercially-available conductive filaments made of polylactic acid (PLA) containing graphene or carbon black as conducting agents have been proposed.[1] However, recent publications have reported the presence of metallic impurities (Fe, Ti and Al) in commercial filaments of graphene/PLA, such as Black MagicTM, which can be accessible after a chemical treatment of the 3D printed surface with dimethylformamide (immersion for 15 min). These impurities affect the electrochemical properties of the 3D-printed material, such as for water splitting.[2] In this context, we demonstrate the electrochemical synthesis of iron hexacyanoferrate (Prussian blue) by cyclic voltammetry in the presence of ferricyanide using iron impurities present in such 3D-printed graphene/PLA electrodes as the iron source. It is well known that Prussian blue (PB) films can be formed electrochemically in the presence of iron (III) cations and ferricyanide. In this procedure, the iron (III) source is provided by the bulky 3D-printed G/PLA electrode after electrode immersion in dimethylformamide for 15 min to remove the excess of PLA and expose iron sites. After continuous voltammetric cycles in a 0.1 mol L^{-1} KCl solution, PB films were grown. Figure 1 shows PB film formed after 50, 100, 150 and 200 cycles. X-ray fluorescence revealed the presence of iron after solvent treatment, in agreement with previous works[2] and Raman spectra confirmed the presence of PB at the modified surface. The generated PB/graphene/PLA electrodes was evaluated for H_2O_2 detection under flow conditions and applying 0.0 V vs Ag/AgCl/KCl_{sat}. The results showed a remarkable performance of this novel platform in the detection of H_2O_2 within a linear range from 1 to 1000 μmol L^{-1} and with a limit of detection of 0.56 μmol L^{-1}. These results are well compared with previously reported electrochemical sensors based on PB-modified electrodes.

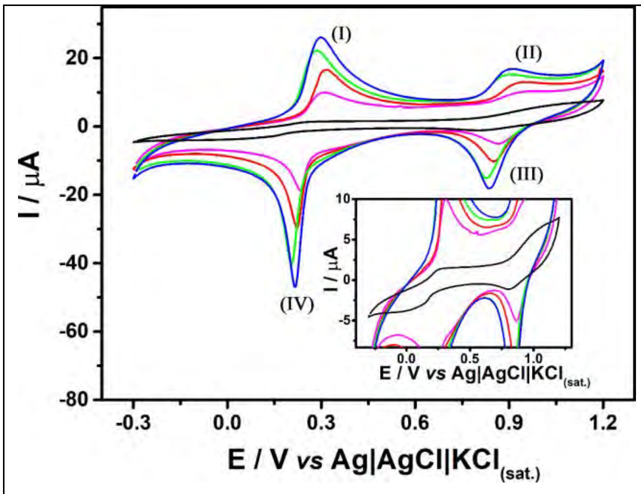

Fig. 1. Cyclic voltammograms in electrolyte of 3D-printed G/PLA electrodes after modification with PB (I and IV correspond to the redox pairs Prussian blue/Prussian white and II and III to Berlin green/ Prussian blue)

Untreated electrode (black line);
DMF treated surface and PB formation after 50 cycles (pink line);
After 100 cycles (red line);
After 150 (green line) and after 200 cycles (blue line).
Scan rate: 50 mV s^{-1}; Step potential: 5 mV; Electrolyte: 0.1 mol L^{-1} KCl + 0.01 mol L^{-1} HCl.

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How Can Details of Processes of Conducting Polymers Be Uncovered by Means of In-situ Combined Electrochemical Techniques

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Since the discovery of electronically conducting polymers, not only their large-scale of potential applications has been evidenced, but many of them have been already put on realization. To improve functioning of such polymer based devices, the multi-faceted cognition of these materials is indispensable. Especially, the elucidation of their redox switching between non-conducting and conducting states is of prime importance. In situ electrochemical techniques are widely applied to study this phenomenon, because they deliver extra information about the processes from an additional aspect, such as spectral modifications, mass, structural, volume and conductivity changes, occurring in parallel with either the electropolymerization process or the redox transformation of the film. A recent book [1] was dedicated to the advantages of such combinations. Moreover, recent technical developments have led to combination of two in situ analytical methods to extend further the understanding of the redox behavior of conducting polymers by furnishing information on the self-same polymer film from several aspects at the same time by employing two in situ electrochemical techniques in a hyphenated mode.

This contribution intends to present examples how fundamental questions can be answered by designing and performing adequate experiments.

Answer to the question and longtime uncertainty whether the chain growth takes place via a coupling between two cation radicals or in a reaction of the cation radical with the monomer could be answered by UV-VIS spectroelectrochemistry.

A series of spectrally followed polymerizations revealed that the film has to be left to relax before its first electrochemical reduction, in order to avoid irregularities and irreversible damages. Parallel EQCM, in situ conductance and pH changes indicated that still existing protonated segments are transforming during the relaxation.

An extraordinary cation exchange behaviour evidenced by EQCN measurements has been found with poly(3,4-ethylenedioxythiophene), synthesized in the presence of chloride or fluoride ions. Thus, the idea of simple charge compensation role of the counter ions has to be completed by eventual specific interaction of the charge carrier with the dopant.

Voltabsorptiometric data during the first section of the return from the conducting state indicated a dissociation-type step in both anodically and cathodically doped films.

Role of the formation of optically distinguishable charge carriers in the development of the conducting state have been studied by using the hyphenation of spectroelectrochemistry with in situ conductance. It has been evidenced that fast redox switching – essential for practical applications - is expected only with polymers doped by immobile anions.

Sophisticated use of these techniques are not restricted to studies on conducting polymers, but can be extended for all kinds of electroactive layers.

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Imaging Effects of Hyperosmolality on Individual Tricellular Junctions

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Transport process across the blood-brain barrier (BBB) takes place by either transcellular pathways or passive paracellular pathways. At cell-cell junctions, paracellular pathways consist of tight junctions (TJs) regulated by TJ proteins to protect the brain from harmful substances in the blood. However, some drugs related to neurological cares are known to transiently upset TJ proteins which disrupt the integrity of the BBB, such as hyperosmolar agents, the drugs of a major treatment for intracranial hypertension resulted from brain trauma. Thus, it is of great importance for people to fully understand the effects of these drugs on TJs to inform current therapies of possible side-effects. To measure the effect of a specific drug on paracellular transport, techniques using Ussing chamber and two-path impedance spectroscopy can be utilized to monitor paracellular conductance/resistance. While informative, they are not able to collect characteristic responses from a single cell, or the permeability change at small but important subcellular structures like tricellular TJs (tTJs). In this study, we utilized potentiometric-scanning ion conductance microscopy (P-SICM) conductance mapping to provide nanometer scale analysis of the response of the TJs at Madin–Darby Canine Kidney strain II (MDCKII) cells to hyperosmolar agent mannitol, from which tTJs and its counterpart bicellular TJs (bTJs) can be visualized and differentiated. We discovered that hyperosmolar condition (termed hyperosmolality here) leads to increased conductance at tTJs without significant alteration in conductance at bTJs. To quantify this effect, an automated computer vision algorithm was designed to extract and calculate conductance components at both tTJs and bTJs. Additionally, lowering Ca^{2+} concentration in the bath facilitates tTJ disruption under hyperosmolality. Strengthening tTJ structure by overexpressing immunoglobulin-like domain-containing receptor 1 (ILDR1) protein abrogates the effect of hyperosmolality. We posit that osmotic stress physically disrupts tTJ structure, as evidenced by super-resolution microscopy. Findings from this study not only provide a high-resolution view of TJ structure and function, but also can inform current osmotherapy and drug delivery strategies for brain diseases.

Applications of scanning electrochemical microscopy for high-resolution imaging and chemical sensing of corrosion reactions and corrosion protection strategies

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Scanning electrochemical microscopy (SECM) has become a very powerful tool for the investigation of solid-liquid interfaces in corrosion processes. Corrosion processes are initiated in micrometer and sub-micrometer ranges, and they are usually very heterogeneously distributed on the surface of the reacting metals. In situ and real time monitoring thus requires the use of spatially resolved techniques such as scanning electrochemical microscopy (SECM). The movement of an ultramicroelectrode (UME) in close proximity to the interface under study allows the application of various experimental procedures that can be classified into amperometric and potentiometric operations depending on either sensing faradaic currents or concentration distributions resulting from the corrosion process. Quantitative analysis can be performed using the UME signal thus revealing different sample properties and/or the influence of the environment and experimental variables that can be observed on different length scales. In this way, identification of the earlier stages for localized corrosion initiation, monitoring of water and specific ions uptake by intact polymeric coatings applied on metals for corrosion protection as well as lixiviation, and detection of coating swelling -that constitutes the earlier stages of blistering-, have been successfully achieved. Prominent examples will be selected to illustrate the selection of operation modes and the problems encountered when working with practical samples.

Hybrid (iso)porphyrin – polyoxometalate copolymer for photo(electro)chemical applications: from flat to mesoporous ITO electrodes

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The development of hybrid polymers incorporating POMs is a promising approach to elaborate new functional materials. To expand the practical applications, their association to a visible-light photosensitizer is needed. In this context, we have developed a method of electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin dications.[1-2] The formation of hybrid POM-porphyrin copolymeric films (Fig. 1, film I) can be obtained by the electro-oxidation of porphyrin in the presence of the POM bearing two pyridyl groups (Py-POM-Py) [3]. This process is feasible for various type of POMs such as Dawson, Lindqvist or Keggin type POMs [4-6].

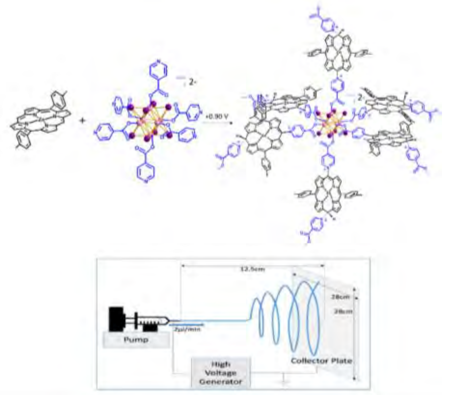

Figure 2 Top: 3D poly-Isoporphyrin-POM copolymer. Bottom: Electrospinning configuration used for deposition. of ITO nanofiber layers.

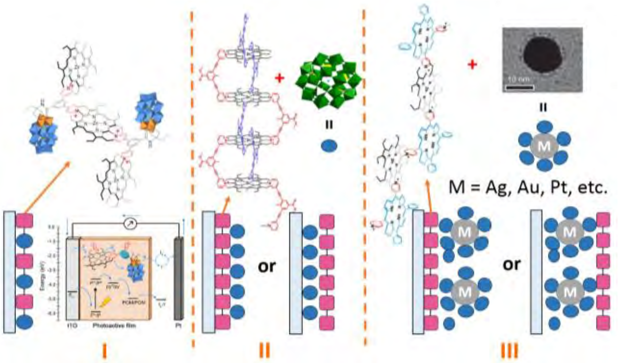

Figure 1 Various type of porphyrin-POM films.

Stable isoporphyrin [7] – POM copolymers (Fig. 2) have been also develop recently showing interesting efficiency even upon the NIR illumination. A second methodology is also proposed to form hybrid POM-porphyrin films (Fig. 1, films II or III): first the formation of cationic polyporphyrin electropolymer. Then, by metathesis reaction, the (partial) exchange onto the surface of the initial counter ions by the POM^{n-} or by the nanoparticles stabilized with POM^{n-} (POM^{n-}@M, M = Ag, Au, Pt, etc.).[8] The photovoltaic performances of these hybrid materials have been investigated by photocurrent transient measurements under visible-light illumination [9-11] given by now good efficiency. In order to increase the efficiency, mesoporous ITO electrodes (nanofiber formed by electrospun or porous ITO electrode obtained using a colloidal co-assembly approach) have been used and will be discussed (Fig. 2).

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Magnetic Field-Driven Extraction of Peptides for Potentiometric Biosensing

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Potentiometric sensors based on polymeric membrane ion-selective electrode (ISE), with attractive advantages of portability, robustness, and resistance to interference from turbidity, have been well developed in the field of biosensors [1]. Peptides have simple and defined structure and exhibit specific and strong affinities to a variety of analytes. Moreover, in contrast to antibodies, peptides are intrinsically more stable in harsh environments [2]. In principle, peptides can be positively or negatively charged, which could induce a potentiometric response on the polymeric membrane ISEs. Inspired by the potentiometric responses of polyamino acids [3], we envision that a general and direct potentiometric sensing platform can be designed by using peptides for both molecular recognition and signal transduction. In this presentation, direct potentiometric assays based on magnetic field-driven extraction of peptides into polymeric membranes will be reported.

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Development of Bioelectrochemical Sensor Based on *Cytochrome bd Oxidase*

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The *cytochrome bd oxidases*, family of unique prokaryotic enzymes from the pathogenic respiratory chain, catalyze the reduction of molecular oxygen in water and oxidation of quinols. It is also found that these proteins play the crucial role in bacterial adaptivity and resistance to oxidative stress which makes *bd oxidases* the promising target for future antibiotics [1]. Here, we developed the enzyme-based electrochemical sensor for the screening of a compound library in order to find effective inhibitors of *bd oxidase* quinone-binding site. The application of the biosensor gives additional information on the catalytic behaviour of *bd oxidase*, immobilized on the 3D gold nanoparticles network which was previously modified by self-assembled monolayer of 6-mercaptohexan-1-ol and hexanthiol. The stability of protein films was tuned by adding lipids, varying the protein concentration and different thiols bound to the surface, so the screening results were obtained with good reproducibility [2].

The developed electrochemical sensor was successfully applied for the natural antibiotic Aurachin D and its synthetic derivatives screening, molecules that resemble the quinone scaffold. It was shown that the halogen substituent at 3-position is not influential, however, the length-dependent isoprenoid chain in this position plays crucial role in activity of potent inhibitors. Additionally, the role of Ubiquinone as cofactor was investigated for better understanding of the *bd oxidase* catalytic mechanism.

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Selective Electrochemical Control of the Fluorescence of Biomolecules: a Strategy to Monitor their Distribution Across Vesicular Lipid Architectures

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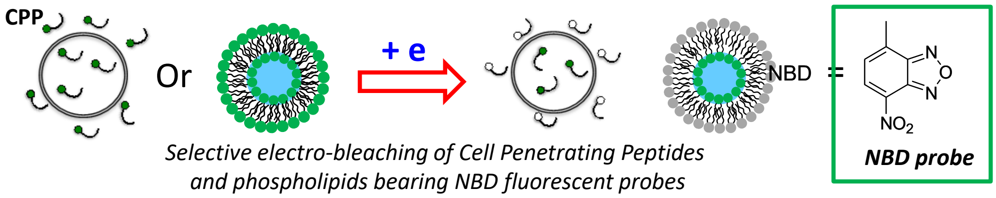
Transport of bioactive molecules across cell membranes is a central issue for living organisms since they encompass crucial processes including cell signaling and communication, cellular excretory activity and drug delivery. In this context, the development of instrumental methodologies possessing both high temporal and spatial resolutions to investigate transmembrane trafficking is still requested. The combination of amperometry and fluorescence is a representative example of the benefits brought by sensitive and time-resolved techniques in the exploration of vesicular exocytosis.[1] Based on this strategy, we recently explored the implementation of electrochemical commands to control fluorescence in order to study the passive transport of bioactive molecules across membranes.[2-4] Accordingly, we have shown that the fluorescence emitted by NBD-labelled biomolecules (NBD=7-nitrobenz-2-oxa-1,3-diazole) can be quenched electrochemically, a key property to study the trafficking of cell penetrating peptides (CPP). More specifically, we showed that such an electrochemical command is a powerful approach to discriminate internalized and non-internalized peptides incubated with purely lipidic nanometer-size vesicles. Interestingly, this strategy has also proved efficient to selectively switch off the fluorescence emitted by NBD-labelled phospholipids localized only on the outer leaflet of vesicles.



Selective electro-bleaching of Cell Penetrating Peptides and phospholipids bearing NBD fluorescent probes

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Coupling Electrochemistry and Photocatalytic Activity of Dissolved Molecular Photosensitizers in Organic Medium

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Photosensitizers and photocatalytic reactions attract lots of attention due to a high demand for green technologies in organic synthesis, water and air purification, energy conversion. Moreover, new photosensitizers find applications in photodynamic therapy, artificial photosynthesis, biochemical studies as ROS generators, and in newly emerging fields such as photoelectrochemical sensing. Thus, discovering photosensitizers with advanced performances and evaluation of factors influencing their activities are crucial.

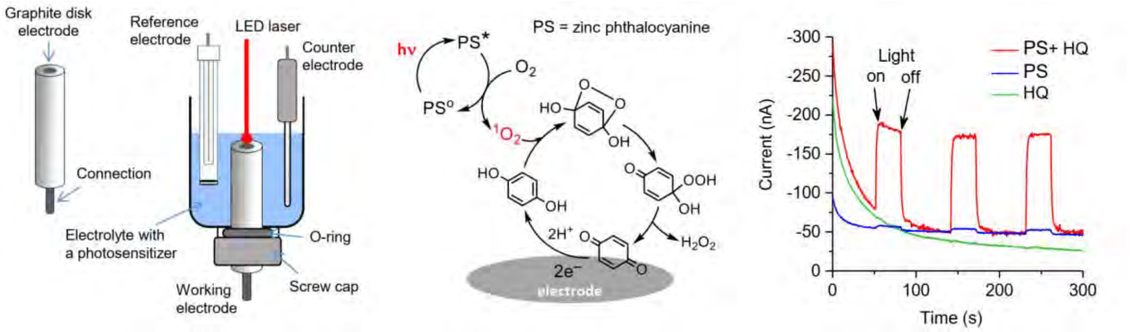

Fig. 1. Schematic illustration of the photoelectrochemical cell and the redox cycling mechanism

In the presented study [1], we developed a fast amperometric method to test the photocatalytic activity of type II photosensitizers dissolved in methanol making use of the redox cycling of hydroquinone (EC_{cat}-mechanism, Fig. 1). Within the suggested detection scheme, photocatalytic oxidation of hydroquinone is followed by amperometric reduction of the oxidized product (benzoquinone) at a graphite electrode giving rise to a photocurrent that can be linked to the rate and quantum yield (Φ_Δ) of singlet oxygen ($^1O_2$) generation. The method is suitable for measuring high $^1O_2$ quantum yields ($\Phi_\Delta >0.5$) as well as low yields ($\Phi_\Delta <0.05$) in the same experimental conditions and time scale. Moreover, the system does not require accumulation of a reaction product since the amperometric signal develops near instantly when the light is on, which enables dynamic monitoring of a photosensitizers' activity at varying conditions in a single experiment.

Besides the demonstrated application in characterization of photosensitizing activity, this work also represents the first example of one-pot coupling of electrochemical and photosensitized reactions in an organic medium.

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Electrochemical Surface-enhanced Infrared Absorption Spectroscopy of Nitric Oxide Reductase Immobilized on Gold Electrodes

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Nitric oxide reductases (NORs) are a transmembrane metalloenzyme and catalytically reduce NO to N_2O in the microbial denitrification process. This enzymatic reaction occurs at a binuclear active center of the non-heme Fe_B and the heme b_3,[1] and the reaction mechanism remains unclear even though it has been intensively studied using physicochemical techniques including protein film electrochemistry.[2]

We have combined protein-film electrochemistry (PFE) and surface-enhanced infrared absorption (SEIRA) spectroscopy of a cytochrome *c*-dependent NOR (*c*NOR). The cNOR isolated from *P. aeruginosa* was immobilized on a SEIRA-active gold film electrode on hemicylindrical Si prism via self-assembled monolayer (SAM) of functional group-terminated alkylthiols and then the addition of phospholipids produced a protein-tethered lipid bilayer membrane (ptBLM), which was tracked by time-resolved SEIRA spectroscopy. The formation processes of BLMs were surely dependent on the existence of protein immobilized on SAMs. Potential-dependent SEIRA spectra at the *c*NOR-immobilized Au electrode, where the enzyme was almost exposed to the aqueous electrolyte solution, enabled us to assign the reduction potential of the binuclear active center, which revealed that heme b_3 involves the enzymatic NO reduction.[3] However, the effect of surrounding BLMs has not been included in the previous study. To gain further mechanistic insights, potential-dependent SEIRA spectroscopy at the ptBLM-immobilized Au electrode under NO is underway.

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Perovskites as electrocatalyst for glycerol oxidation: reaction pathway

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Biodiesel, a biofuel, have faced a constant increase on its production by attending the demand for sustainable fuel. The increase on its production have led to an excess of glycerol, a co-product of biodiesel production, in global market in a way that its use as fuel and/or precursor for value-added chemicals can be consider at the same time that high pure hydrogen can be produced in a electrolyzer.[1] Noble metal as Pt, Au, Pd and Ag have demonstrated its activity to oxidize glycerol[2] but the materials cost turns their use unviable[2]. Thus, to enable this type of device, it is extremely important the development of low cost electrocatalysts.

Perovskite oxide materials can be considered as an option of electrocatalysts. This kind of material has demonstrated being active as catalyst for glycerol reform in heterogeneous catalysis[3] and as electrocatalyst for glycerol and methanol oxidation for solid oxide fuel cell (SOFC).[4,5] Thus, in this work, we present the first findings of $LaNiO_3$ and $LaCoO_3$ as electrocatalysts for glycerol electrooxidation reaction (GEOR) suggesting a reaction pathway supported by *in situ* FTIR and sample collection *online* coupled to HPLC.

Figure 1(a1 and a2) shows the voltammetric profile of GEOR on both materials. $LaNiO_3$ (a1) and $LaCoO_3$ (a2) are active for GEOR and $LaCoO_3$ does not suffer with poisoning during cycling. The obtained currents for $LaNiO_3$ are c.a. 250 times higher than those for Ni/C[6].

Figure 1(b1 and b2) shows the *in situ* FTIR results. Bands due to the formation of formic (1580, 1380 and 1350 cm^{-1}) and glycolic (1580 and 1075 cm^{-1}) acids during GEOR are observed for both electrocatalysts. In the case of $LaCoO_3$ the presence of oxalic acid (1308 cm^{-1}) can also be observed. *Online* HPLC experiments corroborates the *in situ* FTIR results demonstrating the formation of formic and glycolic acid, being formic acid formed in higher amounts on $LaCoO_3$.

These results show that perovskite oxides are active for GEOR, producing high specific currents and the generation of formic and glycolic acids.

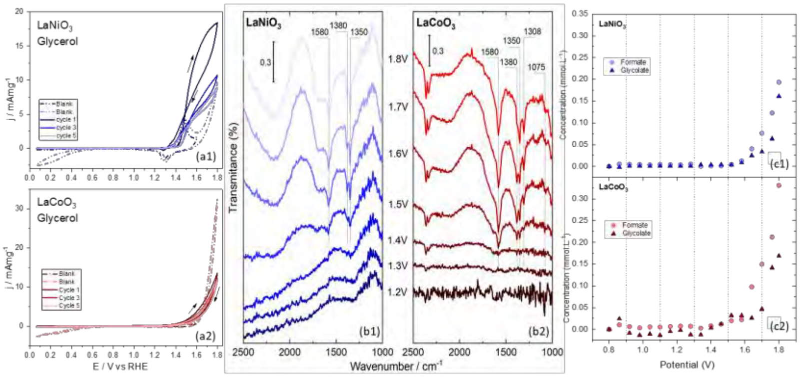

Figure 1: Voltammetric profile for GEOR on $LaNiO_3$ (a1) and $LaCoO_3$ (a2) (blank in dashed line). FTIR spectra of $LaNiO_3$ (b1) and $LaCoO_3$ (b2) collected in SNIFTIRS (reference 0.8V). Formate and glycolate formation detected by *on line* HPLC for $LaNiO_3$ (c1) and $LaCoO_3$ (c2). All results in a solution of $0.1 molL^{-1}$ glycerol in $0.1\ molL^{-1}$ NaOH.

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An enzyme-free H2O2 sensor based on poly(2_aminophenylbenzimidazole)/gold nanoparticles coated pencil graphite electrode

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A poly(2-aminophenylbenzimidazole)/ gold nanoparticles (P2AB/AuNPs) coated disposable pencil graphite electrode (PGE) was fabricated as an enzyme-free sensor for the H_2O_2 determination. P2AB/AuNPs and P2AB were successfully synthesized electrochemically on PGE in acetonitrile for the first time. The coatings were characterized by scanning electron microscopy, X-ray diffraction spectroscopy, Energy-dispersive X-ray spectroscopy, Surface-enhanced Raman spectroscopy, and UV-Vis spectroscopy. AuNPs interacted with P2AB as carrier enhances the electrocatalytic activity towards reduction of H_2O_2. The analytical performance was evaluated in a 100 mM phosphate buffer solution at pH 6.5 by amperometry. The steady state current *vs.* H_2O_2 concentration is linear in the range of 0.06 to100 mM (R = 0.992) with a limit of detection 3.67×10^{-5} M at - 0.8 V *vs.* SCE and no interference is caused by ascorbic acid, dopamine, uric acid, and glucose. The examination for the sensitive determination of H_2O_2 was conducted in commercially available hair oxidant solution. The results demonstrate that P2AB/AuNPs/PGE has potential applications as a sensing material for quantitative determination of H_2O_2.

Elucidating reactions of individual nanoparticles by electrochemical dark-field microscopy

Albeit nanoparticles, especially silver and gold, are frequently used to date in medicine and sportswear due to their antibacterial and anti-inflammatory properties, their physical properties, chemical reactivity and degradation are still poorly understood. Single noble metal nanoparticles can be studied with dark-field microscopy based on their localized surface plasmon resonance (LSPR). H, it is possible to observe their optical appearance (color) and scattering spectrum by hyperspectral dark-field imaging. Hyperspectral imaging can be used to observe a change of the LSPR *operando* due an applied potential and a subsequent electrochemical reaction by monitoring the scattering intensity and spectrum

With this new technique, further insights into reaction dynamics and processes or structural transformations of nanoparticles during their electrochemical reaction can be obtained [1-3]. Hence, this knowledge can be used to gain more information about the *operando* properties of nanoparticles itself and the effect of the dielectric environment in the vicinity of the surface of the particles.

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Hierarchical *“Core-Shell”* Low-Loading Pt Oxygen Reduction Reaction Electrocatalysts Based on a Graphene *“Core”* and a Carbon Nitride *“Shell”*

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Electrochemical energy conversion and storage (EECS) devices are expected to play a crucial role towards the achievement of a sustainable energy system at the global level. Among EECS, a particularly high relevance will be enjoyed by proton exchange membrane fuel cells (PEMFCs). In these EECS, the electrooxidation of hydrogen by oxygen yields a direct current without the emission of greenhouse gases [1]. The process is highly efficient, but is bottlenecked by the sluggishness of the oxygen reduction reaction (ORR) [1]. To ensure that the PEMFC achieves a performance level compatible with the intended application, the ORR must be promoted by suitable electrocatalysts (ECs). Platinum is the most promising material for the active sites of such ECs. However, to place PEMFCs closer to market and to prevent supply bottlenecks the total amount of noble metal needs to be curtailed.

This work overviews the development of a new family of low-Pt ECs for the ORR, whose active sites are found on the surface of sub-nanometric clusters (SNCs) where Pt is alloyed with a first-row transition metal (*e.g.*, Ni, Cu) that operates as a *“co-catalyst”* and raises the intrinsic performance of each active site much above the Pt baseline [2].

The SNCs increase the utilization of Pt atoms included therein by up to *ca.* one order of magnitude with respect to the Pt nanoparticles (NPs) adopted in state-of-the-art ORR ECs, thus raising the specific power yielded by the PEMFC. Values as high as 14 kW/g_{Pt} are achieved, that exceed the target set by the DoE for 2020 (*i.e.*, 8 kW/gPt).

The support of the low-Pt ECs described herein exhibits a *“core-shell”* morphology, including a hierarchical graphene-based (H-GR) *“core”* that is covered by a carbon nitride (CN) *“shell”*. H-GR consists of highly defective graphene nanoplatelets and carbon black NPs [3], to facilitate mass and charge transport. The CN *“shell”* includes less than 5 wt% of N (to prevent the introduction of ohmic drops) and though C- and N-based ligands makes up *“coordination nests”* that, together with defects of the graphene, stabilize the SNCs resulting in an outstanding durability of the ECs.

This report takes into consideration the various families of low-Pt ECs based on H-GR supports developed so far by our group, and compares the interplay between the preparation parameters (in particular the type of support) and the physicochemical properties with the electrochemical behavior and the performance in a single PEMFC tested under operating conditions.

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Increasing Microbial Fuel Cell Power Densities Requires a Better Understanding of Factors that Impact Electrode Performance

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Improving power generation of microbial fuel cells (MFCs) requires that the systems are optimized to reduce resistances that limit system performance. Through quantification and analysis of these factors we were able to modify the cell design, and produce a maximum power density of 7.1 ± 0.4 W m^{-2} in 100 mM phosphate buffer (PBS), the highest power density ever generated for an MFC to our knowledge. The reactor was a flow-through cell with an anion exchange membrane (AEM) separating anode and cathode (all 7 cm^2) in a membrane electrode assembly (MEA) configuration. Through analysis of factors impacting the electrode resistance, we minimized the total internal resistance by using a felt anode, AEM, and cathode tightly packed together specifically to enhance the hydroxide ions transport from cathode to anode and minimize pH imbalances and solution resistance (R_Ω). Therefore, in 50 mM PBS the MFC produced one of the highest power density recorded in such media, with 5.7 ± 0.4 W m^{-2} (at 29 ± 1 A m^{-2}, internal resistance of 7.2 ± 0.6 mΩ m^2), and 25% higher in 100 mM PBS.

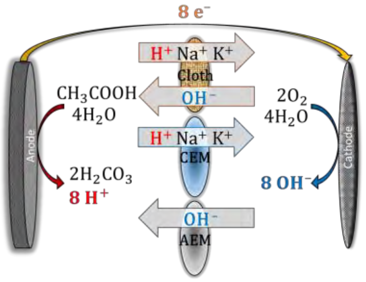

Fig. 1. Comparison of the ion transport in MFCs with a cloth separator, CEM, or AEM. Note that the cathode reaction is balanced by release of hydroxide ions and not consumption of protons. Only the AEM can selectively enhance hydroxide ion transport from the cathode and thus control charge balance through OH^- transport rather than H^+ ion transport.

In contrast to other MFCs using a cation exchange membrane (CEM) in MEA configurations, an AEM facilitate hydroxide ion transport. The carbon felt anode and an air cathode (no catholyte) were pressed onto the AEM, ensuring an electrode spacing similar to the membrane thickness (106 ± 1 μm) and facilitating transport of only the hydroxide ions produced at the cathode by the oxygen reduction reaction (ORR) while water diffuses through the membrane (Figure 1). Cation transport was severely limited by using an AEM while hydroxide anion transport was enhanced by the localized concentration gradient and the electric field at high current densities. Oxygen intrusion in the anolyte was limited by maintaining a low humidified air flowrate. To further minimize internal resistance the anolyte flow was directed through the felt anode to improve overall performance. Maintaining the anode and cathode close together contributed in minimizing R_Ω to only 1.09 ± 0.02 mΩ m^2, compared to R_Ω > 14 mΩ m^2 for a cubic MFC with brush anode and air-cathode [1]. To maximize overall power production in MFCs, the protons produced at the anode and the hydroxide ions produced at the cathode need to be transported towards the other electrode, to effectively obtain a neutral pH and avoid acidification of the anodic biofilm [2].

Our MFC design using an AEM placed directly on the cathode minimized the total solution resistance, selectively transferred hydroxide ions from the cathode to the anode, and thus better neutralized protons produced at the anode lowering internal resistance and substantially improving the reactor performance.

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On the thermodynamics of electroactive microorganisms

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Electroactive microorganisms (EAM) are capable of performing extracellular electron transfer (EET). It represents a unique metabolic trait enabling the exchange of electrons via cytochromes across the cell membrane with solid electron conductors (e.g., electrodes). Although EAM attracted considerable interests over the last decade, their thermodynamic characterization is still in its infancy. However, assessing the energy fluxes during EET is a prerequisite for deciphering their ecological role and for leveraging their biotechnological potential. Yet, a comprehensive thermodynamic analysis of EAM requires a profound understanding of their energy conversion.

Therefore, the peculiarity of the electron-transport chain (ETC) and the energy harvest of EAM is discussed. As metabolically received electrons are transferred across the cell membrane, a certain share of ETC components is located in the periplasm and at the outer membrane. Thus, they cannot contribute to the generation of proton motive force across the inner membrane subsequently utilized for ATP synthesis. Consequently, the question arises, to which extent the anode potential influences the energy harvest of EAM. By applying a previous developed model for electroactive biofilms[1], it is illustrated that the anode potential indeed influences the reaction conditions for substrate oxidation. However, this is solely a kinetic effect while the thermodynamic frame of EAM is not affected by the anode potential[2]. Therefore, energetic assessments require an adapted approach compared to classical thermodynamic calculations.

Furthermore, bioelectrocalorimetric studies with *Geobacter anodireducens* enrichment cultures are performed for measuring the heat dissipation during EET. By analyzing redox titration experiments, the so far unknown microbial electrochemical Peltier heat (mePh) was revealed. It represents an entropic effect at the cytochrome/solid electron acceptor interface for direct EET and amounts in the studied model system to a heat formation of −27±6 kJ per mole of transferred electrons[3]. The mePh constitutes a metabolic trade-off as it decreases biomass yield but provides driving force for growth. To further assess this novel effect, alternative electron acceptors are analyzed.

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Bioelectrochemistry to improve biological gas desulfurization

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The biological gas desulfurization process under haloalkaliphilic conditions is widely applied in industry for removal and conversion of H_2S from sour gas streams, such as biogas and natural gas. his continuous process consists of two steps: 1) Selective absorption of H_2S into a (bi)carbonate solution in an absorber column and 2) conversion of sulfide to elemental sulfur by sulfide oxidizing bacteria (SOB) in an aerated bioreactor. One of the challenges in this process is to increase the selectivity for sulfur formation, by decreasing the production side-products thiosulfate and sulfate, to reduce the requirements of NaOH to keep alkalinity. To increase this selectivity, the continuous biological desulfurization process was extended with an anaerobic bioreactor, which was placed in between the absorber and aerated bioreactor. It was hypothesized that both the biological formation of sulfate as the chemical formation of thiosulfate would reduce as a result of incubation of the SOB under the sulfidic conditions in the anaerobic reactor. With the anaerobic bioreactor, a selectivity for sulfur formation of 97% was achieved, compared to 75-80% without anaerobic bioreactor. This lead to a reduction in NaOH consumption and bleed stream formation of 80-90%. A surprising finding was the ability of SOB to remove part of the sulfide from solution in the anaerobic bioreactor. We hypothesized that SOB can shuttle electrons from sulfide from the anaerobic bioreactor to the aerobic bioreactor.

To study the hypothesis of electron shuttling, we performed batch experiments to study two processes: 1) the removal of sulfide from solution and 2) the release of electrons from SOB at the anode in an electrochemical cell. We used bioreactor solutions from two biological desulfurization systems; one from a full scale plant) with absorber and aerated bioreactor, and one from a pilot plant) with additional anaerobic bioreactor. We found that SOB removed all sulfide from solution when exposed to concentrations up to 0.2 mM^2. After SOB were transferred to an electrochemical cell, they released electrons to an anode in absence of free sulfide. Average current densities of 0.48 and 0.24 A/m^2 were measured for bioreactor solutions with two different types of SOB, at +0.1V vs Ag/AgCl. Current was negligible for reactor solutions without SOB. The recovered charge increased with more positive anode potentials. We hypothesize that SOB can oxidize sulfide to sulfur under anaerobic conditions and store electrons in e.g. the form of reduced quinones and cytochromes.

Another challenge in the desulfurization of sour gas streams is the presence of organosulfur compounds (thiols). These compounds inhibit SOB and as a result, gas streams with a high thiol concentration cannot be treated in an efficient way. We developed a bioelectrochemical process for the degradation of thiols to sulfide at the cathode. Methanethiol, ethanethiol, propanethiol and dimethyl disulfide were supplied separately to the cathodes of bioelectrochemical systems. These systems were controlled at a constant current density of 2 A/m^2 and 4 A/m^2. We observed removal of thiols, and a considerable part of the total sulfur added in the form of thiols was recovered as sulfide: 18% for methanethiol and ethanethiol, 17% for propanethiol and 22% for dimethyldisulfide. No sulfide was formed in electrochemical nor biological control experiments, demonstrating that both current and microorganisms are required for the conversion of organosulfur compounds. With further development of this process, the applicability of the biodesulfurization process can be extended to sour gas streams with high thiol content.

The combination of high pH and high salinity, the fact that bacteria can produce electricity in the absence of free sulfide, and the possibility to degrade thiols at biocathodes, offers new opportunities for design of biological desulfurization systems and bioelectrochemical reactors.

Electrochemical Deposition of Composite and Hybrid Materials

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The formation of well-controlled composite and hybrid material layers is challenging. One would wish to control not only the thickness but also the organization on the nanometer and micrometer scale, and the composition of such coatings. Furthermore, for many applications the layer should be deposited on complex geometries, such as screws, springs, tubes, etc. Finally, the incorporation of organic materials, such as drugs, makes it even more challenging and avoids the application of high-temperature methods, such as CVD, high-temperature spraying and more.

Electrochemistry is an ideal method for controlling the deposition of a wide variety of materials on conducting surfaces. Yet, typically electrochemical deposition is based on the oxidation or reduction of molecular species on the electrode surface and the formation of less soluble species that therefore, deposit instantaneously on the electrode. This does not allow good control on the formation of nanomaterials and even less composite and hybrid materials.

We have developed during the last years a different approach that is based on the deposition of nanomaterials and macromolecules from their dispersion onto the electrode surface upon applying an electrochemical potential.[1-4] This approach, which we term from "nano to nano" is based on destabilizing the dispersed nanomaterials in the solution causing them to precipitate because of applying an electrical potential. As the potential drives the deposition, it allows controlling the thickness and composition of the deposit, in case that co-deposition takes place. This enabled us to form graded layers, to co-deposit organic and inorganic materials, polymers and nanoparticles and much more. Moreover, deposition could be accomplished on a variety of surface topographies, and therefore, was applied for coating medical implants, grids and conductive patterns.

The lecture will give an overview of this exciting field and discuss future perspectives.

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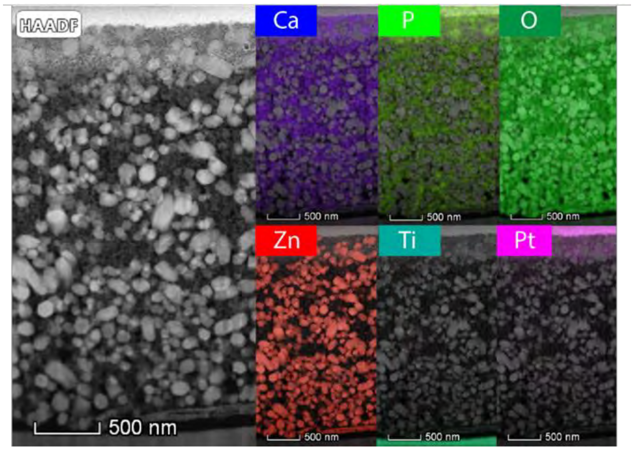

A graded deposition of hydroxyapatite and ZnO by controlling the applied potential (from ref. 3)

Signal Amplified Sandwich-type Photoelectrochemical Assay Based on Polypyrrole/g-C_3N_4/WO_3 Inverse Opal Photonic Crystals Triple Heterojunction

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Photoelectrochemical (PEC) analysis, as a promising and fast-growing technology, has attracted widespread attention for biomedical molecules and environmental pollutants detection due to its high sensitivity, low cost and low background noise [1]. In PEC sensors, the photoactive materials are core component, which play a vital role in the conversion of excitation photoirradiation to responsive electrochemical signal [2]. In recent years, tungsten oxide (WO_3), known as a visible light response semiconductor, has been widely used in the field of PEC detection, owing to its chemical and thermal stability [3]. However, the detection sensitivity of pure WO_3 photoelectrode is still limited by its relatively low photoelectric activity with the high photo-generated carriers recombination rate and low light absorption efficiency. Notably, to overcome above issues, the construction of heterojunction can be an efficient strategy in the inhibition of photo-induced electron-hole pairs recombination [4]. Especially, the formation of inverse opal photonic crystals (IOPCs) in photoactive materials can enhance the optical response of PEC system, attributing to the light trapping structure with uniform and periodic pores surrounded by solid walls [5]. Therefore, a novel sandwich-type PEC sensing platform based on polypyrrole/g-C_3N_4/WO_3 inverse opal photonic crystals (PPy/g-C_3N_4/WO_3 IOPCs) triple heterojunction was proposed in our studies [6]. The sandwich-type recognition system can not only enhance the sensitivity, but also favor the assembly the heterostructure. Benefiting from the appropriate cascade band-edge levels, the heterojunction among PPy, g-C_3N_4 and WO_3 highly accelerate the separation of photo-generated charges. Meanwhile, WO_3 IOPCs can greatly increase the light absorption of PEC detection electrode. With the simultaneous combination of these techniques, the developed PEC sensor possesses great photoelectric property and exhibits high sensitivity with low limit of detection (LOD) as 0.004 nM ($\approx$ 1.99 ng L^{-1}) towards oxytetracycline (OTC) in water. The excellent selectivity and satisfactory detection results in real sample further revealed the potential of the signal amplification strategy integrating the semiconductor IOPCs with its heterojunction structure assembled through sandwich-type detection model for PEC analytical application.

Acknowledgements
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Electrochemical Detection of Metabolite Biomarkers Using Nanomaterials Modified Carbon Electrodes

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The levels of metabolites generated in human metabolism are related to human health conditions can be used for disease diagnosis. Herein, we introduce our latest research works focusing on creating electrochemical sensing platforms for three metabolite molecules, which can be used as a disease biomarker individually, i.e., inosine (INO), hypoxanthine (HX), and dopamine (DA). For the detection of cardiac ischemia biomarkers, INO and HX, a layer-by-layer (LbL) process involving a positively charged polyelectrolyte and negatively charged enzyme self-assembled on a screen printed carbon electrode (SPCE) was designed; LbL assembled polysaccharide chitosan and enzyme purine nucleoside phosphorylase [1] for INO, whereas poly(diallyldimethylammonium chloride) coated carbon nanotube-graphene complexes and enzyme xanthine oxidase for HX [2]. In addition, a combined use of poly(L-methionine), carbon nanotube-graphene complexes, and Au nanoparticles [3] on SPCEs was developed for DA of which level is related to Parkinson's disease and pheochromocytoma. Surfaces of three different electrode configurations were carefully characterized using various surface sensitive analytical tools including scanning electron microscope, atomic force microscopy, energy dispersive spectroscopy, and X-ray photoelectron spectroscopy. Under optimized conditions, each electrochemical sensors described above were applied separately to analyses of INO, HX, and DA in buffer and human biological fluid sample solutions using cyclic and differential pulse, and square wave voltammetric techniques. The sample analysis results were finally validated by comparing to those using liquid chromatography-mass spectrometry and/or commercially available assay kits.

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Lab-on-a-chip device for parallel optical and electrical detection of antibiotics

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Antibiotic drugs are widely used in our society and healthcare system. Unfortunately, the massive use of drugs causes anti-microbial resistance. The antibiotics Vancomycin hydrochloride (Van) is a typical 'last resort' antibiotics, which is used to treat a number of different bacterial infections. It is most effective against Gram-positive bacteria such as Methicillin-resistant Staphylococcus aureus (MRSA), which can cause very severe and sometimes fatal infections and is one of the major problems in clinical routines. Administration of Van is recommended intravenously to treat serious infections by Gram-positive bacteria such as in complicated skin infections, bloodstream infections, endocarditis, bone and joint infections, and meningitis caused by Staphylococcus aureus.

For the correct dosing of Van during therapy, companion tests of blood concentration levels are recommended, a technique called theranostics – therapy with combined diagnostics. Theranostic monitoring is important to avoid possible side effects due to excessive overdosing such as nephrotoxicity or ototoxicity. Underdosing should be avoided as well, since Van as one of the last possible medication options should effectively kill bacteria in patients with severe health condition. Since monitoring of Van has to be done daily or even several times per day, this is a typical application for a theranostic device for point-of-care usage. A biosensor for Van at bedside could help to provide patients always with the right dose, thereby increasing the effectiveness and reducing the side effects of drug treatment.

Here we realized an ultralight analytical biosensor system that, (i) provides an automated fluidic control on-chip, and (ii) combines optical and electrical detection mechanisms, for fast and accurate monitoring of Van in point-of-care settings. Optical detection of Van is carried out based on quenching of nanoparticles catalyzed chemiluminescence (CL) in a concentration-dependent inhibition process. Going beyond enzyme based CL detection schemes such as enzyme linked immunosorbent assays (ELISA), our method makes use of novel Van-specific silver nanoparticle (AgNP) assemblies, produced in a self-assembly based bio-nano conjugation. CL-quenching assays for Van detection require very low sample volumes (20 µL) and show high reproducibility and sensor dynamic ranges (10-15 µg/mL) covering clinically relevant concentration ranges on Van dosing. In parallel, we integrated a metal-microelectrode arrays (MEA) based electrochemical impedance spectroscopy sensor for electrical detection of Van. Here, Van-specific antibodies were immobilized within a fouling resistant polypyrrole matrix on gold microelectrodes using chronoamperometry. Van binding to the antibodies leads to a change in impedance signal, which can be measured in real-time using a miniaturized impedance analyzer and can be reaffirmed from the CL based optical detection.

With this novel Lab-on-a-chip device, we realized a generic opto-electronic biosensor platform, which could be easily adapted to other biosensor assays for point-of-care scenarios, when fast, accurate and automated biomolecule detection is needed.

Nitrosyl-BODIPY dyes: spectroelectrochemical and computational investigations

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BODIPY is an outstanding class of fluorescent dyes with wide applications in biological/analytical/environment research. In this work, the electrochemical properties of new nitrosyl BODIPY dyes (**1-3**) were studied in degassed ACN + n-Bu_4NPF_6, along with computational studies. Compound **1** displayed the usual reduction behavior for unsubstituted BODIPY, while in the oxidation region it showed two irreversible waves (Epa1 = 1.61 V; Epa2 = 1.92 V) (Fig. 1A), probably due to the formation of radical cation and dication, respectively. The addition of the acceptor nitroso group, in compound **2** (Fig.1 B) and **3** (Fig. 1C), leads to a different profile. The reduction is much easier, ca 460 mV more positive for compound **3**. The first to be reduced is the nitroso group, due to the proximity to the positively charged N (EpIc$_3$ = -0.281 V), and non-bonding interactions with the electronegative borondifluoride, differently from compound **2**, with a β-nitroso group, where the reduction occurs in the BODIPY core (EpIc$_2$ = -0.408 V). In the oxidation region, the irreversible peaks for compound **2** (Epa = 2.00 V) and **3** (Epa = 1.96 V) respectively, may be related to the formation of radical cations in the NO group. ωB97xD/cc-pVTZ results had shown that the HOMO orbitals are mainly formed by the π orbitals of nitroso group, with a small contribution of orbitals from atoms of the ionic form of pyrrole ring of BODIPY moiety. A possible chemical interaction between the lone pair of fluorine of BODIPY core and π electrons of nitroso ligand for compound **3**, can be the reason for the slightly higher oxidation susceptibility for it. Comparing the IP calculated by the Koopman's theorem for values for compound **2** and **3** is possible to note that these values are approximately the same (~0.06 eV difference). As shown by electrochemical/computational profiles, the location of the group (α or β) strongly affects the electronic structure, and consequently, their reactivities.

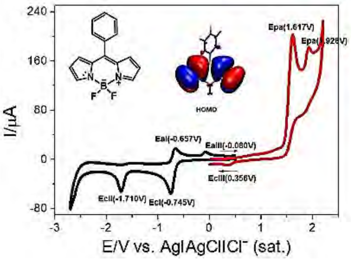

Fig 1A: CV of compound **1.**

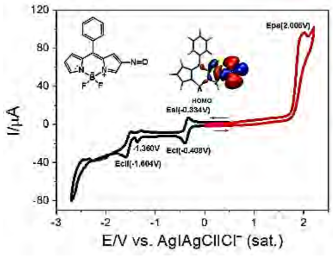

Fig 1B: CV of compound **2.**

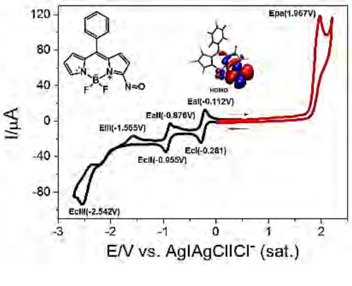

Fig 1C: CV of compound **3.**

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Compacts of Synthetic Diamond as Electrodes: Platinum Additive Effect on Their Electroactivity

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Conducting diamond compact composition electrode materials are obtained by graphite transformation to diamond at high pressure and temperature in two- and three-component Pt–C and Pt–C–B growth systems; their physical and chemical properties are studied [1]. The diamond electrode added with Pt in the two-component growth system Pt–C behaves in the chloride-ion anodic oxidation reaction like a purely platinum one, with due allowance for the platinum actual amount at the electrode surface. Results of voltammetric studies are in good agreement with the electrochemical impedance spectroscopy data obtained in f-sweep and E-sweep modes. The boron doping of the diamond grown in the Pt–C–B system produced electrodes electroactive with respect to the chloride-ion anodic oxidation reaction; the electroactivity increased with the increasing of the platinum content at the electrode surface. The adding of platinum (a catalyst) was shown being more efficient (in the chlorine anodic evolution reaction) when the platinum was deposited right onto the electrode surface, rather when introduced to its bulk during the compact synthesis.

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Knowledge-based AI for Smart Design of Functional Nanoparticles in Non-vacuum Reactive Environment

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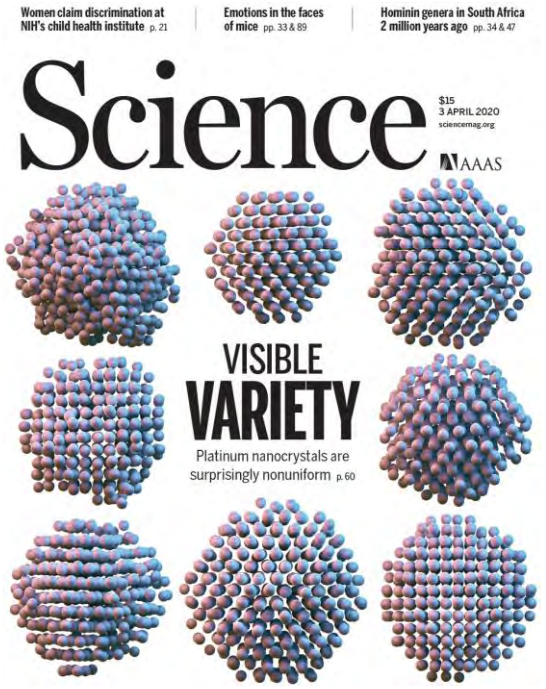
Nanomaterials have been played a key role in wide range of electrochemical energy devices such as Li-air batteries, photovoltaic devices, and fuel cells. Innovative design for highly functional nanoparticles has been, however, delayed. In molecular level computational electrochemistry new research paradigm has been established, which substantially incorporates IT-based artificial intelligence (AI) technology into machine learning algorism. Using the new computational methodology high-throughput screening of promising nanoparticle candidates has been attempted for various desired applications.

Whether the frontier approach is successful or not is significantly controlled by the reliability and accuracy of input database. It is true that substantial amounts of the data are come by previous literatures and often ab-initio calculations with idealized model systems. The conditions in which the data were generated may be so different from the operando circumstances of the target materials. To secure extreme-level integrity of the database the in-situ measurement of nanoparticle structures should be carried out, from which the reliable correlation of the structure-performance-design principle can be identified.

We combined in-situ TEM measurement of nanoparticle with ligand in liquid and AI-based neural-network approach to precisely establish three-dimensional (3D) structure database. The information includes sizes, lattice distortions, and defects with picometer resolution under non-vacuum conditions. From the 3D liquid-cell electron microscopy atomistic interaction potential and surface reactivity are analyzed using density functional theory calculations and machine learning techniques. The approach is indeed 'knowledge-based' AI, which can be expected to make groundbreaking ways toward the quantum nanoarchitecture.



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Investigating Solid-State Synthesis Reactions By In Situ Synchrotron X-Ray Diffraction And Ab Initio Thermodynamics

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In the synthesis of inorganic materials, reactions often yield non-equilibrium kinetic byproducts instead of the thermodynamic equilibrium phase [1]. Why is that? And why, on the other hand, compounds predicted as thermodynamically stable often cannot be synthesized experimentally? Understanding the competition between thermodynamics and kinetics is fundamental for answering these questions and towards the rational synthesis of target materials [2]. In this presentation, we will highlight the use of in situ synchrotron x-ray diffraction to yield insights on the real time behavior of powder precursors during synthesis. We investigate the multistage crystallization pathways of the important two-layer (P2) sodium oxides $Na_{0.67}MO_2$ (M = Co, Mn) [3]. We find a series of fast non-equilibrium phase transformations through metastable three-layer O3, O3' or P3 phases, before formation of the equilibrium two-layer P2 polymorph. A theoretical framework to rationalize the observed phase progression will be presented, demonstrating that even though P2 is the equilibrium phase that we target, the first phase to form will be the one with the most negative compositionally-unconstrained reaction energy from the powder precursors. In other words, the first phase to form is guided by thermodynamics and it does not necessarily have the composition corresponding to the overall precursor composition in the reaction vessel. Afterwards, the first phase may develop according to kinetic or thermodynamic arguments, depending on the system of choice. Further examples will be presented for industrially-relevant $LiNiO_2$ and related compounds [4], where lithiation pathways can be instead more straightforward than sodiation ones; nonetheless, the high resolution of synchrotron XRD allows to observe detailed structural information revealing a complex behavior where metal vacancies play an important role. The insights we present constitutes a step forward towards unraveling the complex interplay between thermodynamics and kinetics during synthesis. Moreover, they can guide the choice of precursors and parameters towards the optimization of the solid-state synthesis of ceramic materials.

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Novel Verdazyl Electrolyte for Symmetrical Non-aqueous Redox Flow Batteries

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All-organic redox-flow batteries (RFBs) as an emerging branch of energy technology offer a modern and benign solution for buffering energy obtained from renewable but intrinsically intermittent sources. The "heavy duty" nature of battery application dictates a persistent need for new battery chemistries where precisely tailored physicochemical properties of redox electrolytes are utmost preferred [1]. In light of this, verdazyl free radical compounds stand for promising candidates for symmetrical all-organic RFBs due to variety of synthetic ways to adjust their structure as well as unique bipolar feature, enabling a single redox molecule for both negolyte and posolyte. Concurrently, an irreversible exchange of electrolytes within a cell gets appropriately prevented [2].

The presented work comprises preliminary screening of verdazyl compounds library in respect of bulk diffusion coefficient and heterogeneous electron transfer rate constant as the key redox electrolyte parameters, by means of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). In line with this, within a given set of symmetrical electrolytes, the best performing verdazyl-based radical was identified for RFB experiments in order to compare an electrochemical behavior (CV) within an actual cell and prerequisite data and thereafter confirm a viability for energy storage (galvanostatic cycling experiments) as well as to characterize a redox electrolyte from different angles within a single cycle ("state of the charge" experiments). Due to the fact that structure of the redox-flow cell significantly differs from the electrochemical one used throughout the preselection, a study of the present setup transition was conducted as well.

In the scope of long-term galvanostatic cycling experiments, symmetrical verdazyl electrolyte demonstrated good stability and high Coulombic (>97%) as well as energy efficiencies for more than 100 charge/discharge cycles. On this account, obtained results highlight verdazyl-based electrolytes as promising and versatile energy material and implies a wide field for further synthetic development and optimization in the field of RFBs.

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From Nanoelectrochemistry to Real-Time Biosensors: Analysis of Neurotransmitters Using Nanoporous Electrode

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The emerging biosensing devices largely extend our capability to measure and monitor the biomolecules in living organisms. Yet most commercially available detection platforms are either simplified for a handful of abundant molecules in vivo, *e.g.*, glucose and electrolytes, or designed with time-consuming sample pretreatment for low-abundance targets. There is an urgent quest to integrate the advancement of analytical chemistry and nanotechnology to solve the long-existing problems for biodetection. In this talk, I will first present a novel electrochemical detection platform that consists of high-density nanoscale electrodes, *viz.* nanopore electrode arrays (NEAs), for single entity detection by integrating into lab-chip device setting. I will describe a robust fabrication method to achieve nanopores with zero-dimensional structures and discuss how permselectivity and ion migration are well-positioned to explore in situ molecular separation and detection. Next, I will present a real-time sensing technology to measure neurotransmitters in the living brain using the nanoporous electrode. So far, the widely used technique for *in vivo* brain measurement is through fast-scan cyclic voltammetry, which cannot measure non-redox active species, and requires frequent drift-correction and complicated data analysis. The biosensor developed in this work is capable of continuously measuring the neurotransmitters from the cerebrospinal fluid of the animal brain. This biosensor is designed on the flexible substrate with highly specific bioaffinity recognition elements for chronic multisite brain recordings. Overall, this talk will depict a general approach to access real-time chemical information for a better understanding of the brain functions.

Engineering Redox Mediating Systems to Study Photoinhibition Effects of Exogenous Mediators in Purple Bacteria

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Microbial (photo)electrochemical systems offer outstanding possibilities, spanning from sustainable (micro/low) power generation, biosensing of toxic compounds, bioelectrosynthesis of valuable chemicals, and bioremediation of contaminated environments. However, they also provide a unique platform for the study of the electrochemical processes at play between abiotic and biotic components. To date, achieving a detailed understanding of the electron transfer process between intact bacteria cells and an exogenous electron acceptor remains one of the biggest challenges in microbial electrochemistry.[1, 2] For the specific case of photosynthetic microorganisms, an additional challenge for studying the electron transfer process is posed by the confinement of their photosynthetic apparatus in membranes located inside their cells, thus physically separated from the electrode surface. In recent years, multidisciplinary approaches have proven effective in gaining insights into these complex systems. Specifically, electrochemical studies have been coupled to computational methods (i.e., modeling, bioinformatics, and quantum mechanic calculations),[3, 4] fluorescence techniques,[5] as well as the engineering of both the biotic and/or the abiotic components,[6] expanding our understanding of bio-photoelectrochemical systems.

Herein, purple bacteria are utilized as model photosynthetic organisms based on their extremely versatile metabolism and capability to adapt to environmental stresses,[7] which would enable their application for semi-artificial photosynthesis in the field. Various reports on the harvesting of photoexcited electrons from the photosynthetic apparatus of purple bacteria indicated that exogenous redox mediators are required to successfully establish a photocurrent, where both Os-based and quinone-based mediators were employed.[8, 9] However, over long term experiments, the use of exogenous mediators can lead to photoinhibition, resulting in decreasing photocurrent generation. With the aim to study photoinhibition effects of exogenous quinone mediators, we explored the use of an artificial, bio-inspired redox polymer and its corresponding monomeric diffusible redox moieties. The approach allowed unveiling different mediator-photosystem interactions, and the effects of diffusion and electron transfer limitations on the resulting photoinhibition,[10] providing directions for the rational design of artificial redox mediating systems for enhancing both photoexcited electron harvesting and the stability of the system.

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Structural and Electrochemical Characterization of Lithium and Transition Metals Polyanionic Compounds

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The importance of autonomous energy is currently growing due to the rapid development of portable electronic devices, electric vehicles and power supplies for distributed energy systems. Combinations of various energy storage devices such as a battery, a fuel cell and a supercapacitor can be used to expand the range of operating modes of energy sources in terms of power and energy intensity. Among the electrochemical systems used in batteries, a lithium-ion system (lithium-ion battery, LIB) stands out, which is significantly ahead of other systems both in terms of characteristics and degree of development. At the same time, this system has significant potential for further development. The most numerous and diverse electrode materials are LIB's cathode materials. Having achieved notable success with oxide compounds of lithium and transition metals, the researchers turned their attention to a much wider class of polyanionic compounds, promising comparable energy intensity and significantly higher chemical stability and safety at operation. The electrode potential of intercalation compounds increases in the series of polyanions: SiO_4^{4-}, BO_3^{3-}, PO_4^{3-}, SO_4^{2-}. At the same time, intercalation compounds with various polyanions have a significant scatter in the values of theoretical capacity and practical characteristics depending on the composition as well as structural and morphological properties. For the targeted improvement of the electrochemical characteristics of electrode materials, the accumulation and analysis of information on the relationship between the preparation features, structural, morphological and electrochemical properties is necessary (Fig. 1) [1].

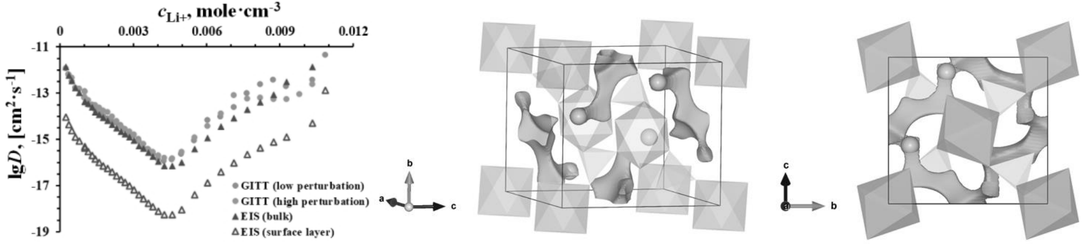

Fig. 1. Concentration dependences of the diffusion coefficient and the calculated diffusion map of lithium ions in the compound $Li_2Fe(SO_4)_2$.

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Solid-state Architecture Batteries for Enhanced Rechargeability and Safety (SABERS)

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All-electric vertical take-off and landing vehicles (eVTOL) for urban air mobility (UAM) concepts face numerous challenging technical barriers before their introduction into the consumer marketplace. The most challenging of these technical barriers to overcome is developing an energy storage system capable of meeting the rigorous aerospace safety and performance criteria. The performance metrics for eVTOL craft, such as specific energy and cycle life, are at least 2 times greater than those of electric automobiles. Furthermore, safety is essential for operation of commercial electric aerovehicles. Preliminary systems level analysis studies have indicated that there are five key properties which must be optimized for successful implementation of battery systems. Those five key criteria are safety, energy density, power, packaging design and scalability. Current state-of-the-art (SOA) lithium-ion batteries meet or exceed the requirements for electric aviation in the areas of power and scalability, yet are insufficient in the key performance criteria of energy, safety and packaging design.

The SABERS concept proposes a battery that meets all five key performance criteria through the development of a solid-state architecture cell design utilizing high energy density and power density sulfur-selenium cathode with a lithium metal anode. Data will be presented demonstrating high performing sulfur - selenium cathode that offers a balanced energy to power density ratio, which can be tailored to the specific application by altering the stoichiometric ratios of sulfur to selenium. This cathode is being developed by implementing NASA patented holey graphene technology as a highly conductive, ultra-lightweight electrode scaffold. Novel processing methods allow developing solid-state electrolyte that is a safe, non-flammable replacement to the highly flammable liquid organic electrolytes currently used in SOA lithium-ion batteries. The all solid-state lithium-sulfur-selenium cell design enables the implementation of a bipolar stack configuration, which has the advantages of reducing overall cell weight, reducing the amount of interfaced connections for the cell, and minimizing cooling requirements for the battery. In particular, the solid-state design allows for a serial stacking configuration to enable dense packaging of the cells within the bipolar stack. Lastly, optimization of battery components occurs through a robust and rigorous combination of various computational modeling techniques covering multiple length scales. The expected result will be a solid-state battery with operational temperatures from 0 °C to 150 °C which provides the required energy density, discharge rate, and inherent safety to meet strict aerospace performance criteria.

Electrolyte and Interface for Calcium Battery

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Various metals have been used as battery anodes in electrochemical cells ever since the birth of the batteries with Volta's pile and in the first commercialized primary (Zn/MnO2, Leclanché 1866) and secondary (Pb/acid, Planté 1859) batteries. Li-MoS2 cells, employing Li metal anodes, with specific energies two to three times higher than both Ni/Cd and Pb/acid cells, were withdrawn from the market due to safety issues related to dendrites growth. Instead, Ca are currently being considered as safer metal anode alternative. [1] Pioneering work by Aurbach et al. in the early 1990's showed a surface-film controlled electrochemical behavior of Ca metal anodes in electrolytes with conventional organic solvents. [2,3] The lack of metal plating was attributed to the poor divalent cation migration through the passivation layer.

Nevertheless, recent demonstration of Ca plating and stripping in the presence of a passivation layer [4,5] has paved the way for assessment of new electrolyte formulations with high resilience towards oxidation. However, several challenges remain to be tackled for the development of Ca based batteries.[1,6] Among these, the need for reliable electrochemical test protocols, mass transport limitations and high desolvation energies (due to strong cation-solvent and cation–anion interactions) are implied.[8,9] Here, a systematic investigation of the electrolyte formulation impact on the cation solvation structure and transport is presented.[10] Finally, characterization of the passivation layer formed onto the Ca metal anode in various electrolyte formulations using complementary techniques will be presented allowing for the identification of the most suitable passivation layer components in terms of divalent cation mobility.

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Understanding and Designing of Materials and Interface for High Energy Batteries

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Abstract: The fast growth of portable power sources for transportation and grid-scale stationary storage presents great opportunities for battery development. How to increase energy density, reduce cost, speed up charging, extend life, enhance safety and recycle are critical challenges. Here I will present 15 year research in my lab to address some of challenges by understanding the materials and interfaces and providing guiding principles for design. The topics to be discussed include: 1) A breakthrough tool of cryogenic electron microscopy, leading to atomic scale resolution of fragile battery materials and interfaces. 2) Materials design to enable high capacity materials: Si and Li metal anodes and S cathodes. 3) Interfacial design with polymer and inorganic coating to enhance cycling efficiency of battery electrodes.

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Proton-Coupled Electron Transfer in Electrochemistry

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Proton-coupled electron transfer (PCET) reactions play a vital role in a wide range of electrochemical processes. This talk will focus on theoretical studies of molecular and heterogeneous electrocatalysis, highlighting the interplay between theory and experiment. A general theory of PCET that includes the quantum mechanical effects of the electrons and transferring protons, as well as the motions of the proton donor-acceptor mode and solvent environment, has been developed. This formulation enables the calculation of rate constants, current densities, Tafel slopes, and kinetic isotope effects for comparison to experiment. The application of this PCET theory to molecular electrocatalysts designed for water splitting illustrates the use of multi-proton relays to transport protons over hydrogen-bonded networks, as well as the ability to tune the redox potentials through substituents and other molecular design strategies. The application of this PCET theory to proton discharge on a gold electrode in acetonitrile explains the experimentally observed potential-dependent kinetic isotope effect in terms of contributions from excited electron-proton vibronic states that depend on both isotope and applied potential. This theory also provides insight into the fundamental principles underlying proton discharge to a gold electrode in acidic and alkaline aqueous solution. These applications highlight the importance of using a vibronically nonadiabatic theory that quantizes the transferring proton and includes the effects of hydrogen tunneling and excited electron-proton vibronic states. Recent periodic density functional theory calculations of electric fields at electrochemical interfaces and PCET at graphite-conjugated acids elucidate the impact of the applied potential on the electronic structure and interfacial fields. The insights from these theoretical studies are useful for the design of both molecular and heterogeneous electrocatalysts to control the movement and coupling of electrons and protons for energy conversion processes.

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Ion-Transfer Stripping Voltammetry of Perfluorooctane Sulfonate

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Per- and polyfluoroalkyl substances (PFAS) are a category of persistent environmental contaminants that have been linked to health issues in humans. In this work, we investigate the detection of perfluorooctanesulfonate ($PFOS^-$), one such PFAS, by ion-transfer voltammetry at an array of microinterfaces between two immiscible electrolyte solutions (μITIES).[1] Cyclic voltammetry, differential pulse voltammetry and differential pulse stripping voltammetry (DPSV) indicated the ion-transfer behaviour and detection of $PFOS^-$, with the latter enabling detection at picomolar concentrations. Using a 5 min preconcentration time, during which $PFOS^-$ was preconcentrated into the organic phase of the μITIES array, a limit of detection (LOD) of 46 pM in aqueous electrolyte was achieved. This performance is attributed to the enhanced mass transport (radial diffusion) to the μITIES that occurs during preconcentration. To investigate the potentiality for applications of this analytical approach to environmental samples, measurements in a range of water matrices were investigated. Drinking water, laboratory tap water and seawater matrices were assessed by spiking with $PFOS^-$ over the 0.1-1 nM range. A matrix effect was observed, with changes in sensitivity and LOD relative to those in pure aqueous electrolyte solutions. Such matrix effects need to be considered in designing applications of these $PFOS^-$ measurements to environmental samples. The results presented here indicate that DPSV at a μITIES array can form the basis for a fast and sensitive screening method for $PFOS^-$ contamination that is suited to portable and on-site applications.

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Catalytically Synthesized Prussian Blue Based Nanozymes Defeating Peroxidase: New Horizons for Electroanalysis

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The term 'nanozyme' is attributed to nanoparticles with enzyme-like activity. Despite the attractive title, the enzymatic specificity, particularly in complex organic reactions, is hardly expectable for nanozymes. Nevertheless, the nanocatalysts with broad specificity can act as the labels or transducers in biosensors. Undoubtedly higher stability of artificial enzymes compared to natural ones, as well as low cost of nanoparticles, explain vivid interest towards nanozymes elaboration. Since peroxidase is probably the most widely used label, a variety of nanoparticles mimicking peroxidase-like activity have been studied.

Among the reported nanozymes, catalytically synthesized Prussian Blue (PB) based nanoparticles are, probably, the only nanozymes suitable for analysis due to their genuine enzymatic properties, including ultrahigh catalytic constant, an absence of oxidase-like activity and an ability to operate in physiological solutions [1]. Synthesis in course of $Fe^{III}[Fe^{III}(CN)_6]$ reduction by hydrogen peroxide, or by conducting polymer forming organic molecules occurs, upon the same reaction as in electrocatalysis. It results in PB structures with the highest catalytic activity, on the one hand, and allows to functionalized nanoparticle surface at deposition step, on the other hand. Such nanoparticles display the size-dependent catalytic rate constants in H_2O_2 reduction, which are significantly improved compared to natural enzyme peroxidase. So, for PB nanoparticles 200 nm in diameter, the turnover number is 300 times higher.

Simple drop-casting of the PB nanozymes suspension with subsequent drying provides improved analytical performance characteristics of the resulting electrochemical (bio)sensors. So, sensitivity of nanoparticles-based H_2O_2 sensors is 30% higher (up to $0.85\ A{\cdot}M^{-1}{\cdot}cm^{-2}$) compared to it for the sensors based on PB films [2]. Optimal sensitivity of the sensors is achieved in case of continuative nanoparticles monolayer (estimated by means of electrochemical impedance spectroscopy [3]) on the electrode surface. Similarly, the use of PB nanoparticles for elaboration of nanozyme-enzyme biosensors provides almost twice higher sensitivity ($> 0.2\ A{\cdot}M^{-1}{\cdot}cm^{-2}$) [4]. The improved analytical performance characteristics of the PB nanoparticles-based (bio)sensors are most probably due to their increased roughness providing more efficient mass transfer compared to conventional PB films.

Further improvement of the signal-to-background ratio peculiar to Prussian Blue is possible using the electrode supports characterized by ultra-low background current, such as boron-doped diamond (BDD). In contrast to PB films deposition using fully oxidized precursors, PB nanozymes immobilization is not detriment for the BDD surface and retains its termination. Compared to conventional graphite electrodes modified with Prussian Blue nanoparticles, the use of BDD provided up to 20 times decreased oxygen reduction currents resulting in 4 times increased signal-to-background ratio [5].

To validate PB based nanozymes as a novel electrochemical label for RNA detection, azido-groups functionalized nanoparticles were successfully conjugated with HULC (Highly Up-Regulated in Liver Cancer) gene sequences. The possibility of nanozymes detection at subnanomolar concentrations in chronoamperometric mode was shown. PB nanozymes conjugated probes are universal and can be used for diverse sensors elaboration.

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Coulometric Transduction for Solid-Contact Ion-Selective Electrodes

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A coulometric transduction method for solid-contact ion-selective electrodes (SCISEs) was introduced by our group in 2015 [1]. Since then, the coulometric method has been explored and optimized further by us [2-5] and others [5, 6]. A key feature of this method is that the potential of the SCISE *vs* the reference electrode is kept constant. Therefore, any potential change at the ion-selective membrane (ISM)|sample interface, due to a change in ion activity in the solution, causes oxidation/reduction of the solid contact. The result is a transient current that is measured and integrated to obtain the charge that is proportional to the change in the logarithm of the ion activity in solution. A unique feature of this coulometric method is that the analytical signal, *i.e.* charge (for a given change in ion activity) is proportional to the redox capacitance of the solid contact, meaning that the signal can be amplified by increasing the thickness (loading) of the solid-contact layer. This is an advantage of the coulometric method compared to classical potentiometry.

The coulometric method has been investigated using poly(3,4-ethylenedioxythiophene) (PEDOT) as solid contact in SCISEs for the detection of K^+ [2-4, 6], H^+ (pH) [4] and Cl^- [5]. The response time of the coulometric method was shortened by lowering the bulk resistance of the ion-selective membrane, either by increasing the geometrical surface area of the electrode [3] or by using spin-coated thin-layer ISMs [4, 5]. A theoretical capacitive model based on a series *RC* circuit gave an excellent explanation of the coulometric response of a Cl^--SCISE [5]. However, impedance measurements showed that the coulometric response for K^+-SCISEs was limited by diffusion even for thin-layer ISMs [4]. An extended theoretical model for the amperometric and coulometric response of K^+-SCISEs, which accounts for concentration polarization in the ISM was recently proposed [6]. Furthermore, coulometric SCISEs were evaluated for measurement of pH in seawater [4] and K^+ in serum [4, 6].

A further electrochemical study of the coulometric response and the corresponding charge transfer processes of Pb^{2+}-SCISEs and Ca^{2+}-SCISEs strengthened our understanding of the coulometric transduction mechanism. Electrochemical characterization of Pb^{2+}-SCISEs with different thicknesses of PEDOT, as well different thicknesses of ISMs, showed that the coulometric response of the Pb^{2+}-SCISE was limited by charge (ion) transport in the PEDOT solid-contact layer. This was explained by interactions between Pb^{2+} and PEDOT doped with poly(styrene sulfonate).

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Enhancement of microbial fuel cell performance by introducing a nano-composite cathode catalyst

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Microbial fuel cell (MFC) is a promising bioelectrochemical device that converts chemical energy into electrical energy through the catalytic reaction of microorganisms in (circum)neutral media at room temperature. Inside the MFC, the electroactive bacteria at the anode oxides the organics generating electrons and protons. Thus, generated protons transfer directly to cathode through the electrolyte while the electrons get transferred through the external circuit generating electricity. Electrons and protons get consumed at the cathode for reducing the oxygen. Unfortunately, the performance of MFCs are limited by several factors that hinder its large-scale applications such as high materials costs, the poor red-ox electrochemical performances and the relatively low durability of the electrodes. For the large part of the scientific community, one of the greater bottlenecks is related to the oxygen reduction reaction (ORR) at the cathode. Despite several oxidant options investigated in MFCs, oxygen is the most preferred solution due to its natural availability in the atmosphere at no additional cost and its high electrochemical potential. However, ORR suffers from its sluggish kinetics mainly due to the low operational temperature and the neutral pH. In order to maintain the biological activity at the anode neither the temperature nor the pH can be varied.

To improve the sluggish kinetics of ORR and the electrochemical performance, catalysts need to be used. ORR catalysts can be mainly classified into 3 categories i) platinum-based materials (PGM), ii) carbonaceous materials, and iii) platinum group metal-free (PGM-free) materials. Platinum-based ORR catalysts (PGM) have been extensively in use in the past but their high cost and low durability have significantly lowered their utilization. Various carbonaceous materials have been in use in MFCs due to their characteristic properties such as low cost, high durability, high electrical conductivity and mechanical strength. However, their performance as catalysts is not high enough, and the ORR kinetics still remains low. PGM-free catalysts (M-N-C) based on transition metals (e.g. Fe, Co, Ni, and Mn) are atomically dispersed on a carbon/nitrogen matrix. It was shown that PGM-free have superior performance compared to AC and Fe-based material is the most performing catalyst [1].

In this work, we investigated the electrocatalytic activity of Fe-AAPyr (Fe-Aminoantipyrine) and 3D-graphene nanosheet (3D-GNS) separately and physically combined for ORR along with AC control. 3D-GNSs were synthesized using a modified Hummers method technique and Sacrificial Support Method (SSM) while Fe-AAPyr was prepared using sacrificial support method with silica template and aminoantipyrine as an organic precursor (C-N matrix). The ORR activity of these catalysts at different loadings was investigated by using rotating ring disk (RRDE) electrode setup in the neutral electrolyte and then the catalysts were investigated in MFC by integrating them into air-breathing cathode. The co-presence of GNS (2 $\mathrm{mgcm^{-2}}$) and Fe-AAPyr (2 $\mathrm{mgcm^{-2}}$) catalyst within the air-breathing cathode resulted in the higher power generation in MFC of 235 ± 1 $\mu\mathrm{Wcm^{-2}}$ while Fe-AAPyr catalyst itself showed high performance (217 ± 1 $\mathrm{mWcm^{-2}}$), higher compared to GNS (150 ± 5 $\mu\mathrm{Wcm^{-2}}$) while AC generated power of roughly 104 $\mu\mathrm{Wcm^{-2}}$ [2].

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Coupled Mass Spectrometry Techniques in Research on Stability of Electro- and Photoelectrocatalysts

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Long-term durability of electrochemical energy conversion devices such as fuel cells and water electrolysers can only be achieved through utilization of stable components. In particular, durable electrocatalysts are required. It is a common practice that on the way to their potential application in real devices, electrocatalysts are typically evaluated in various accelerated stress tests. Unfortunately, even positive results do not guarantee durable performance of the devices, as many degradation processes go unnoticed in such tests. Coupled mass spectrometry techniques were designed to address this issue [1]. Tiny amounts of gasses or dissolved ionic/atomic species formed as a result of a degradation process can be detected using electrochemical gas mass spectrometry (gas MS) and on-line inductively coupled plasma mass spectrometry (on-line ICP-MS), respectively.

Since such techniques are still relatively rare in the electrocatalysis research, this talk will be started with a short introduction on basic operational principles of electrochemical MS in stability research. It will be shown that gas MS and on-line ICP-MS can be used in fundamental mechanistic studies. Moving to examples, dissolution processes in the state-of-the-art Pt/C and IrO_x catalysts and how they have assisted in understanding of catalysts degradation will be described [2, 3]. In order to demonstrate the versatility of the coupled mass spectrometry techniques in fundamental stability research, other representative examples will include: (a) light induced dissolution of Ir photoelectrocatalyst covered WO_3 photoabsorbers [4]; oxidative leaching of sulfur from Pt single atom catalysts; Cu leaching at pHs of interest for carbon dioxide reduction; degradation of non-noble metal fuel cell catalyst, etc. Moreover, novel approaches on application of on-line ICP-MS in more applied gas-diffusion-electrode (GDE) systems will be shown [5].

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Simultaneous Electrochemical Detection of Important Advanced Glycation End Products Involved in Oral Pathology From Raw Saliva

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The pathology of oral cavity is closely correlated with dietary intake. Advanced glycation end products (AGEs) are associated with the processed food and thus, can be ingested by consuming these types of food items. The majority of AGEs, such as methylglyoxal (MGL) and N-(carboxymethyl)lysine (CML) are considered markers involved in oxidative stress by producing long-term damage to proteins in ageing, atherosclerotic plaques and diabetes. AGEs are usually detected using ELISA, immunohistochemistry or HPLC, methods that require long time for analysis and implicit delayed diagnostic results 1,2. A novel approach for the sensitive electrochemical detection of MGL has been elaborated based on a lab-made printed platform using a flexible plastic foil as support, an Ag/AgCl conductive ink for the design of the reference electrode and the contacts, and a carbon ink for the working and counter electrodes. After drying, the surface of working electrode was decorated with a nanostructured platinum film that was generated electrochemicaly using cyclic voltammetry (CV) in the presence of hexachloroplatinic acid in hydrochloric acid. All the steps involved in the elaboration of the sensor were optimized based on the differential pulse voltammetry (DPV) signal of the target analyte. The optimized nanocomposite platform was then characterized using microscopic and electrochemical techniques. The selectivity tests performed for MGL have proved that the presence of CML in the same solution does not hinder the detection. Furthermore, the oxidation signal of CML was not influenced by the presence of MGL. The disposable sensor was successfully tested for direct electrochemical detection of MGL and CML using DPV. The employment of composite electrodes exhibits electron-mediating effect, which leads to a well-defined reduction peak associated to the MGL and a well-defined oxidation peak associated to the CML. The developed assay was shown to be selective and sensitive for the simultaneous analysis of salivary MGL and CML in healthy volunteers even when tested in vivo, being promising for the elaboration of point-of-care devices for salivary analysis.

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Scanning Gel Electrochemical Microscopy (SGECM) for Corrosion: Methodology, Instrumentation and Prospects

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Scanning electrochemical probe techniques, such as scanning electrochemical microscopy and scanning droplet cell techniques (including scanning electrochemical cell microscopy) have been widely applied for studying localized corrosion processes. Recently, we reported the Scanning Gel Electrochemical Microscopy (SGECM) for measuring the topography and corrosion activity of metallic samples placed in air[1,2]. The concept is based on a gel probe that scans over the sample surface in tapping mode. The gel probe is fabricated by electrodeposition of chitosan on micro-disk electrodes or sharpened metal wires (**Figure 1**). It is approached to be in contact with the sample surface by either shear force or current feedback, which confines the electrochemical reactions in the contact area. So far, local amperometry, potentiometry, cyclic voltammetry as well as patterning have been achieved on a home-built SGECM setup with software written in VB.net (**Figure 2**)[1-3].

SGECM offers the following advantages for corrosion applications: (1) The sample is placed in air, making it suitable for studying atmospheric corrosion; (2) The electrolyte is immobilized so that it is applicable to samples of any complex shape; (3) The non-destructive soft contact between the gel and the sample protects the sample to a maximum extent; (4) The instrumentation is automated and foreseen to be miniaturized for field tests. With the recent development, the lateral physical resolution of SGECM reaches *ca.* 1-2 µm, which is already close to the crystalline phases of alloys. Moreover, by pressing or pulling the gel probe after touching the sample surface, the resolution is tuneable in the range of a few to tens of microns. These advantages make SGECM a promising tool for characterizing localized corrosion, as well as fixing coatings or pits at microscale. In this presentation, we will introduce the methodology and instrumentation of SGECM, as well as discuss about prospects and seek collaborations in the corrosion electrochemistry community.

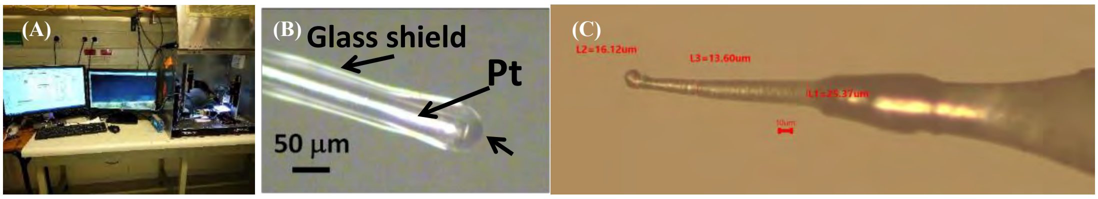

Figure 1. (A) Home-built SGECM setup; Gel probes fabricated by electrodeposition of chitosan on micro-disk electrodes (B) and sharpened metal wires (C).

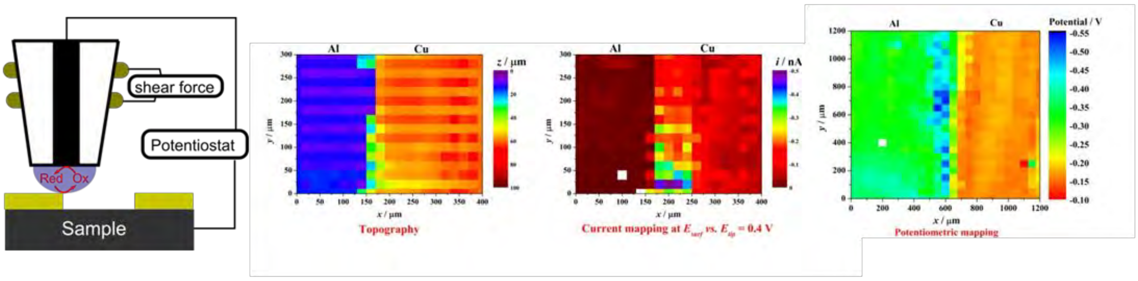

Figure 2. Scheme of SGECM and topography, current and potentiometric (conducted at a different area) mapping of a copper tape on aluminum substrate.

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Prussian Blue based nanozymes “artificial peroxidase” in (bio)sensors

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In modern biotechnology and analytical chemistry peroxidase is apparently the most widely used enzyme. On one hand, it is used as a label in immuno- and DNA-sensors. On the other hand, it is the key enzyme to detect hydrogen peroxide including biosensing purposes.

More than 25 years ago we discovered ferric hexacyanoferrate, as the most advantageous electrocatalyst for hydrogen peroxide reduction. In neutral aqueous media favorable for bioanalytical applications, the advantages of Prussian Blue modified electrodes over the conventionally used platinum are: (i) 3 orders of magnitude higher activity in H_2O_2 reduction and oxidation in terms of the 1000 times higher electrochemical rate constants, obviously providing the similarly improved sensitivity, and (ii) 3 orders of magnitude higher selectivity in hydrogen peroxide reduction allowing low-potential H_2O_2 detection even in the presence of oxygen.

We’ve synthesized Prussian Blue nanoparticles through catalytic reaction involving hydrogen peroxide activation. Prussian Blue is known to be similarly a highly active electrocatalyst in H_2O_2 reduction and in its oxidation. Hence, synthesis of the highly active catalyst for one reaction (H_2O_2 oxidation) would provide its improved catalytic activity also in H_2O_2 reduction. From this point of view, the best reductant for ferricianide−ferric ion mixture would be hydrogen peroxide. Indeed, since precipitation of Prussian Blue in this case requires oxidation of H_2O_2, the most catalytically active structures would have the highest growth rate and, thus, would grow predominantly. As a result, the most catalytically active structures, also in H_2O_2 reduction, would be synthesized [1].

The resulting nanoparticles display the size-dependent catalytic rate constants in H_2O_2 reduction, which are significantly improved compared to natural enzyme peroxidase: for PB nanoparticles 200 nm in diameter, the turnover number is 300 times higher; for 570 nm diameter nanoparticles, it is 4 orders of magnitude higher. Comparing to the known peroxidase-like nanozymes, the advantages of the reported PB nanoparticles are their true enzymatic properties: (i) the ultrahigh activity, which is up to 4 orders of magnitude higher as compared to the enzyme peroxidase, (ii) enzymatic specificity (an absence of oxidase-like activity) and (iii) an ability to operate in physiological solutions. These unique properties allow to denote the catalytically synthesized PB nanoparticles as nanozymes ‘artificial peroxidase’. Together with high stability and low cost, obviously peculiar to noble metal free inorganic materials, the mentioned properties would allow the substitution of natural and recombinant peroxidases in biotechnology and analytical sciences [1].

Simple drop-casting of the catalytically synthesized Prussian Blue nanoparticles with subsequent annealing results in modified electrodes with high electrochemical and electrocatalytic activity. The electroactive fraction of the deposited Prussian Blue being independent of the surface concentration, is decreased with an increase of the nanoparticles size reaching its lower saturation at approximately 25%. Sensitivity of the corresonding hydrogen peroxide sensor is increased linearly with the amount of Prussian Blue reaching its upper saturation together with formation of continuative film, indicating most probably, a nanoparticles monolayer [2].

In contrast to bienzyme biosensors, we propose the nanozyme-enzyme based ones substituting the enzyme peroxidase with the more active and stable nanoparticles “artificial peroxidase”. The resulting nanozyme-enzyme lactate biosensor displays twice higher sensitivity (> 0.2 AM^{-1} cm^{-2}) compared to the Prussian Blue film based one [3].

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Marcus-Hush Theory for Ultramicroelectrodes Revealed by Electron Tunnelling through Hexagonal Boron Nitride

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Although several experimental confirmations of the Marcus-Hush theory of electron transfer have emerged since its introduction in the 1950s, some interesting predictions remain unverified. This includes implications of this theory for ultramicroelectrodes, put forward by Feldberg in 2010, who predicted that significant deviations from the commonly invoked but less generic Butler-Volmer behaviour are to be observed under certain conditions [1]. However, a suitable experimental system, which would meet all of these conditions, including small electrode size, large overpotentials, slow electrode kinetics, and large reorganization energy, simultaneously, has not been found until a decade later.

We discuss electron tunneling through insulating hexagonal boron nitride (hBN), placed between a graphite electrode and an electrolyte solution of a redox mediator (Fig. 1a) [2]. This system favorably meets all of the conditions posed by Feldberg's analysis. The steady-state voltammograms of $[\mathrm{IrCl}_6]^{3-}$ oxidation and $[\mathrm{Ru(NH}_3)_6]^{3+}$ reduction, their rate constants (Fig. 1b), limiting currents, and transfer coefficients all significantly deviate from the expected Butler-Volmer behavior, in an excellent qualitative agreement with Feldberg's theoretical predictions.

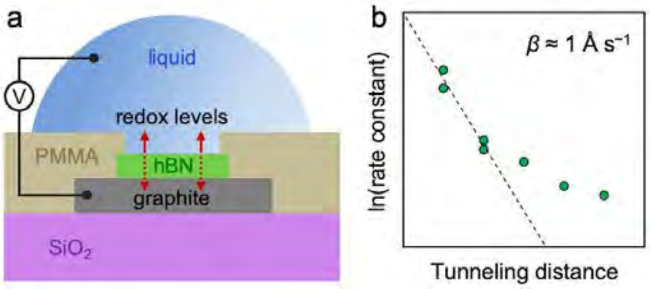

Figure 1: ***a,*** *Schematic of electron tunneling through hBN, between a graphite electrode and redox levels in a liquid.* ***b,*** *Deviation of the heterogeneous electron rate transfer rate constant from the exponential dependence on tunneling distance.*

Beyond another independent confirmation of a fundamental chemical theory, our findings also show that the electrochemical response of a conductive electrode can be effectively tuned by an insulating two-dimensional material of varied thickness. Such tuneability could be exploited in future research on electrode modification, electrochemical switching, or surface passivation [3].

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Electrochemical Hydrogenation of Carbonyl Compounds: The Interaction Between Secondary Functional Group and Electrode and Its Influence on Catalytic Activity

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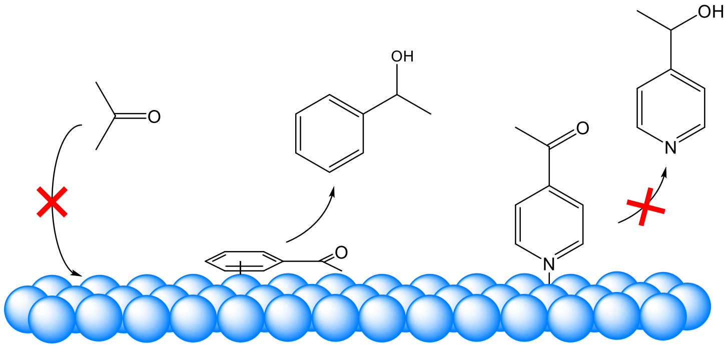

Graphical Abstract: Pt(111) is inactive for the hydrogenation of acetone as the letter will not adsorb. The phenyl ring of acetophenone forces the carbonyl function into a side-on geometry and activates it for the Pt(111)-catalyzed hydrogenation to the corresponding alcohol. 4-Acetylpyridine adsorbs to Pt(111) in an upright position. This makes the carbonyl function inaccessible to the catalyst surface and no hydrogenation can commence.

The heterogeneous hydrogenation of carbonyl compounds in chemical industry is highly relevant for the production of pharmaceuticals as well as fine chemicals. Its electrochemical counterpart has attracted interest, in view of efforts to electrify chemical industry, but also as a means to upgrade biomass derived bio-oils to fuels and platform chemicals. In this presentation we are going to discuss how the interactions between carbonyl compound and electrode surface affects the electrochemical reaction and how it depends on both the surface structure of the electrode and on the molecular structure of the substrate molecule.

Short chained aliphatic carbonyl compounds can only interact with the electrode surface via the carbonyl functional group. In this presentation we are going to show for platinum single crystal electrodes that the coordination number of an adsorption site determines the strength with which the carbonyl functional group adsorbs [1]. Both DFT calculations and experimental results show that acetone does not bind to surface sites featuring high coordination number such as Pt(111) and Pt(100) [1]. The absence of acetone adsorption results in the inactivity of these electrodes for acetone hydrogenation [1]. Adsorption and hydrogenation commences only at step and kink sites with low coordination numbers, whereas the adsorption strength determines whether the hydrogenation yields selectively 2-propanol (at Pt(110)) or in addition propane (at Pt(510)) [1].

Furthermore, we are going to show that adsorption through an inert secondary functional group present in the molecular structure of the carbonyl compound (phenyl ring in acetophenone, pyridine ring in 4-acetylpyridine) can have a strong influence on the reactivity as well. Adsorption through the phenyl ring forces the carbonyl functional group into a site-on geometry at Pt(111). Therefore, Pt(111) is able to catalyze the hydrogenation of acetophenone to the corresponding alcohol, which is not possible in the case of acetone [2]. Adsorption through the *N*-atom of the pyridine ring causes on all platinum surfaces a vertical adsorption mode of 4-acetylpyridine, which creates a physical distance between carbonyl functional group and electrode surfaces, thus inhibiting the hydrogenation reaction [2]. This is even true for Pt(110) which is the most active surface for acetone reduction.

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A H^- Superionic Conductor $Ba_{1.8}LiH_{2.8}O_{0.9}$

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Hydride ions (H^-) can act as charge carrier as they exhibit several features suitable for fast ion conduction: monovalence, moderate ionic size comparable to O^{2-} and F^-, and high polarizability. Furthermore, hydride ions exhibit strong reducing properties through the standard H^-/H_2 redox potential (–2.3 V vs. SHE), which can be expected to be applied to novel electrochemical devices. Following some investigations on H^- conduction in alkaline earth metal hydrides[1-4], we reported H^- conduction in an oxide-based framework structure for the first time by finding a series of H^- conductive oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$[5]. The discovery has triggered exploration of materials for H^- conductors such as K_2NiF_4-type Ln_2LiHO_3 (Ln = Pr, Nd)[6] and Ba_2ScHO_3[7] and fluorite-type $LaH_{3-2x}O_x$[8]. However, a H^- conductor exhibiting both high conductivity and low activation energy had not been developed yet. In the present study, we report a new H^- conductive oxyhydride, $Ba_{1.8}LiH_{2.8}O_{0.9}$, containing a high amount of barium and hydrogen vacancies and exhibiting long-range ordering at room temperature. Increasing the temperature above 315 ºC melts the ordered vacancies (Figure 1), triggering superionic conduction with a high H^- conductivity of over 0.01 $S\cdot cm^{-1}$ nearly independent of the temperature[8]. This is the first report of a H^- superionic conductor, which might open up possibilities for new electrochemical devices.

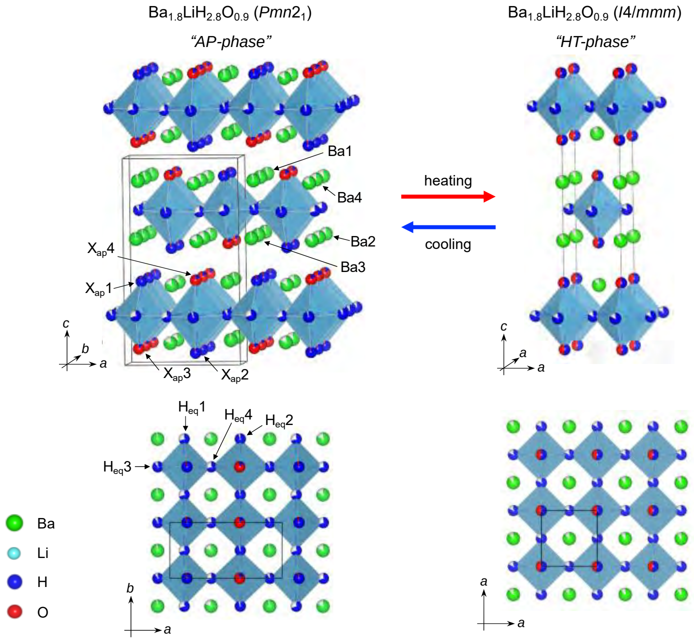

Figure 1. Crystal structures of K_2NiF_4-type $Ba_{1.8}LiH_{2.8}O_{0.9}$. Left: low temperature phase, Right: high temperature phase (high conductivity phase).

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Enantiodiscrimination at electrochemical interphases through implementation of chiral and inherently chiral selectors: novel insights and perspectives

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To achieve enantioselectivity, electron transfer processes at the electrochemical interphase require the presence of a suitable enantiopure chiral selector, resulting in energetically different diastereoisomeric conditions for the two probe enantiomers.[1] A groundbreaking strategy is based on the use of molecular selectors endowed with "inherent chirality", *i.e.* with chirality and key functional properties originating from the same structural element, which in our case identifies with the main molecular backbone, featuring a tailored torsion with a racemization energy barrier too high to be overcome at room temperature. Large peak potential differences have been observed in voltammetry for the enantiomers of even very different chiral probes either (*i*) working in achiral media, on electrode surfaces modified with thin films of inherently chiral electroactive oligomers[1-4] or (*ii*) working on achiral electrodes, implementing inherent chirality in the medium, particularly in ionic liquids ILs, either chiral themselves, or modified by a chiral additive,[1,5,6] exploiting the peculiar IL high order at the interphase with a charged electrode.

Both strategies are being now extended and refined, particularly aiming to collect clues for the elucidation of the recognition mechanism, as well as to highlight attractive applications.

In the film case, we are studying in detail morphology, growth, chemical composition as well as functional properties of inherently chiral electroactive oligomer films, both as electrode surfaces and as self-standing membranes.

In the media case, chiral or inherently chiral molecules are being studied as advanced media and/or media additives/components, with impressive results.

Overall a wide palette of selectors (film or media) and/or probes are being compared, representing four classes of stereogenic elements*, i.e.* stereogenic centres, axes, planes and helixes.

The outstanding enantiodicrimination ability of the new selectors is also being considered beyond molecular chiral probes, *i.e.* towards polarized light components (in terms of circular dichroism and circularly polarized luminescence) and electron spins (in magnetoelectrochemistry experiments). Not only impressive effects have been observed, but fascinating correlations and connections are emerging among the three areas, worthy to be explored in detail, possibly providing further interpretative clues, as well as for possible exploitation in photonics and spintronics..

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Technological advances in CO_2 Electrobiorefinery: Linking Bioelectrochemical CO_2 reduction with Renewable Energy

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Carbon dioxide (CO_2) is considered to be the major cause of climate change by its accumulation in the atmosphere and its greenhouse properties. To counteract climate change, most research focused in the past on Carbon Capture and Storage (CCS). Nowadays it is recognized that rather than just storing it, emitted CO_2 can be a valuable source of carbon for the production of commercially valuable products. This Carbon Capture and Utilization (CCU) approach provides much needed additional capacity in the move towards a low carbon economy.

This presentation focuses on the use of CO_2 as feedstock for the synthesis of chemicals using biotechnology as core process. The main approach to be discussed is microbial electrosynthesis (MES) being used for the production of chemicals using bacteria as electrocatalyst. Already the bioelectrochemical reduction of carbon dioxide to acetate has been achieved as well as the reduction of CO_2 to methane and multi-carbon compounds. The key advantage foreseen here is the use of excess electricity that is often generated renewably such as from solar cells and wind mills, all of which cannot be utilized immediately and can be fed into a MES to produce chemical compounds. Results with specific bacteria towards bioelectrochemical conversion of CO_2 to organic compounds will be reported. Establishment of stable and robust biocathode for the bioelectrochemical CO_2 reduction at the graphite felt cathode succeeded repeatedly under long-term operation which led to the accumulation of higher titer to extractable amount (up to 8-10 g L^{-1} of acetate). When higher titers are obtainable from the CO_2 reduction based MES, product downstream process would be feasible. This requires continuous availability of CO_2 and sufficiently low cathode potential to ensure the supply of reducing equivalents/hydrogen. The dissolution of CO_2 and mass-transfer of reducing equivalents/hydrogen are the main limitations. Improvement on the dissolution and mass transfer rate of CO_2 was explored using gas diffusion electrodes (GDEs). GDE at least doubled the CO_2 mass transfer and MES was able to utilize CO_2 from the diluted gas mixture (20% CO_2) to produce acetate at the rate of 240 mg L^{-1} d^{-1} when the cathode was polarized at -1.1 V/Ag/AgCl.

Microbial electrosynthesis (MES) allow CO_2 capture and utilization for the electricity-driven bioproduction of organics such as acetic acid. Such systems can be coupled to any renewable electricity supply, especially those derived from solar and wind energy. However, fluctuations or even absence of electricity may cause damages or changes in the microbial community, and/or affect the performance and robustness of MES. Therefore, the effect of electric supply interruptions on MES performance was evaluated for the first time initially using bicarbonate as the substrate and later the transformation of gaseous CO_2 into organic products was assessed continuously during 120 days of operation. Time-increasing power outages, from 4 h to 64 h, were applied in order to evaluate the effects of electric energy (current) absence on microbial community, organics formation, production rates and product accumulation. Acetic acid was the main product observed before and after the power outages. In case of bicarbonate as substrate, interruptions affected the acetate production rate, causing a decrease of until 77% after 64 h off. With CO_2 as substrate, a maximum titer and production rate of 6965 mg L^{-1} and 516.2 mg L^{-1} d^{-1} (35.8 g m^{-2} d^{-1}) of acetic acid were observed, respectively.

Pathways Towards Next Generation Energy Storage Technologies Based on Redox Flow Batteries: Solid Boosters and Aqueous Organics

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Redox flow batteries offer interesting options for electrochemical energy storage and even for heat-to-power conversion. In the first part of the talk, we will discuss the possibilities offered by organic redox couples in aqueous solutions,[1] report some recent examples from our lab, and describe our collaborative efforts for computational screening of organic redox couples within CompBat H2020-project.

In the second part of the talk, we shall introduce the concept of solid boosters for flow batteries. The advantage of such systems is that it allows relaxing the requirement for high solubility of the redox couple, significantly increasing the number of redox couples available for flow batteries. Wang et al. first suggested this concept, where the electrolyte tank is filled with solid redox active mm-sized beads forming a backed-bed type system, in 2013.[2] Firstly, the redox mediator is charged in the electrochemical cell and pumped back into the storage tank. The charge is then transferred into the solid material in a chemical reaction with the mediator, similarly to "*molecular wiring*" used, for example, in electrochemical enzymatic glucose sensors exploiting redox mediators to shuttle the electrons between the electrode and the enzyme.[3] The redox mediator can then be further charged in the electrochemical cell. We and others have shown that significant amount of the charge storage capacity of the solid materials can be used with a single mediator, if the redox potentials of the solid and soluble materials match well enough.[4-7] Since charge storage density is much higher in solids, lower concentration of the mediators can be utilized as the capacity of the flow battery boosted with solids is mostly due to the solid only.

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Unveiling the Oxide-based Chemoresistor Sensing Mechanism: When the Theory Meets the Experiment

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The development of high-performing sensing materials, able to detect ppb-trace concentrations of volatile organic compounds (VOCs) at low temperatures, is required for the development of next-generation miniaturized wireless sensors [1-3]. Herein, we present the engineering of highly sensitive chemical sensors, comprising of different Metal Oxide Semiconductors (MOS as ZnO, SnO_2 and WO_3) layouts [4,5]. The chemical properties of these highly porous (> 90%) materials were systematically investigated in terms of composition and morphologies. Then, all the synthesized materials were tested towards different VOC species, namely ethanol (EtOH), acetone and toluene/ethylbenzene (EtBz), in order to eventually highlight the materials diverse selectivity. Optimized layouts demonstrate significant potential as chemoresistors operating at high temperatures (around 300-350 °C) especially in terms of sensitivity, reaching ppb concentrations as the low detection limits (Figure 1a). Furthermore, in order to elucidate the sensing mechanism, experimental *in situ* Modulated Excitation-XANES analyses (at the European Synchrotron Radiation Facilities in Grenoble) along with theoretical studies were carried out (Figures 1b and 1c). Theoretical outcomes reveal the pivotal role played by oxygen species adsorbed on the MOS surface. Hence, the matching of experimental and theoretical results gave us the possibility to hypothesize the possible phenomena at the basis of the sensing behavior.

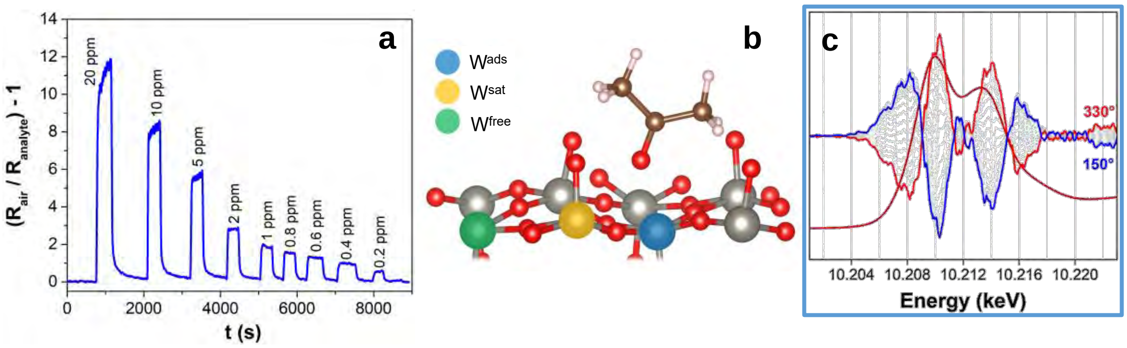

Figure 1. (a) WO_3 sensor response towards acetone; acetone adsorption onto WO_3 nanomaterials on (b) theoretical and (c) experimental (XANES measurements) points of view.

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Enzymatic Reactions versus Electrochemical Transformation of Naphthoyl Indole Derivative

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1-pentyl-3-(1-naphtoyl)indole (hereinafter referred to as "JWH-018") is a compound belonging to a heterogenous group of synthetic cannabinoids, which has recently appeared in the drug market. This substance is abused for its psychoactive effect and serves as alternative to classical drugs (heroin, cocaine, ecstasy) due to its legal status. In human organism, JWH-018 is rapidly and completely metabolized and thus parent compounds are often undetectable. It is necessary to know its metabolism pathway to enable detection of this compound.

In this research, the electrochemical methods were used to study drug oxidation and reduction. Since the electron transfer participates in metabolic pathways, electrochemical behaviour of JWH-018 was studied with purpose to identify short living intermediates of redox reactions. Simultaneously, above mentioned compound was incubated with human liver subcellular fractions (microsomes) and cytochrome. The products obtained by electrochemical and biochemical methods were identified by advanced chromatographic techniques UPLC-MS/MS and serve to identify the potential metabolism of synthetic cannabinoid.

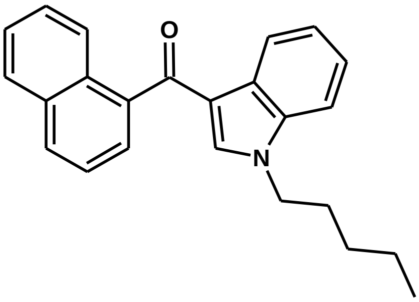

Figure 1: Chemical structure of JWH-018

Acknowledgement

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Deep Eutectic Solvents with Bio-Based Chiral Cations: a New Electroanalytical Approach for the Enantiomeric Excess Determination of Chiral Probes

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The concept of Deep Eutectic Solvents (DES) was introduced by Abbott in 2001. DES are considered as an interesting alternative to molecular organic solvents and ionic liquids. They are constituted by at least two components that interact strongly to form an eutectic mixture. Deep eutectic solvents can be described by the general formula Cat+-X− with Cat+ being ammonium, sulfonium, or phosphonium and X− a Lewis base, in general a halide. DES are usually divided into four types: type I (quaternary salt and metal halide), type II (quaternary salt and hydrated metal halide), type III (quaternary salt and hydrogen bond donor) and type IV (metal halide and hydrogen bond donor). They have different advantages with respect to the other media like: easy, scalable, low cost synthesis; low vapor pressure; non flammability and biodegradability. There are very few works in literature concerning the electrochemistry or electroanalysis of and in DES media regarding the preparation of MIPs (Molecularly Imprinted Polymers), synthesis of nanomaterials, functionalization of carbon nanotubes and film electrodeposition [1]. From 2011 a new class of DES called NADES (NAtural Deep Eutectic Solvents) based on natural molecules was synthetized. In the class of NADES, Chiral Deep Eutectic Solvents (CDES) can be included. CDES were recently synthetized and there are no detailed studies in literature on their physicochemical properties, especially regarding the ones where chirality originates from the cation. The applications on CDES span from the field of catalysis to the one of enantioselective synthesis. They differ from ionic liquids for the possible use on large scale (low cost, low impact on the environment), for the easy synthesis (mixtures of at least two components) and for their composition (adduct between a hydrogen bond donator and a hydrogen bond acceptor). In this work we would like to present a new class of CDES in which the cation is both of natural origin and chiral. The hydrogen bond acceptor is a chiral organic salt of NOPOL-MIM/mesylate, because solid at room temperature and already studied by our group as chiral additive in achiral commercial ionic liquid for the enantiorecognition of chiral probes; the hydrogen bond donators used are the common ones largely employed in literature: glycerol, levulinic acid and urea. Firstly, these CDES were characterized by differential scan calorimetry (DSC) in order to study their physicochemical properties and to determine correctly the eutectic points. Then, we have performed enantioselectivity tests using these additives dissolved in a commercial achiral ionic liquid on plastic and paper screen printed electrodes with different working electrodes (carbon black, graphite and gold), by means of differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). Recorded DPV signals shown a really huge separation between the enantiomers of the chiral analyte in term of peak potential values. For these reason we have decided to test the chiral probes both in enantiopure and in racemic form. We have prepared different mixtures of the enantiomers of the analytes and determined the enantiomeric excesses. Results are really promising, recalling signals obtained as output of a chiral HPLC.

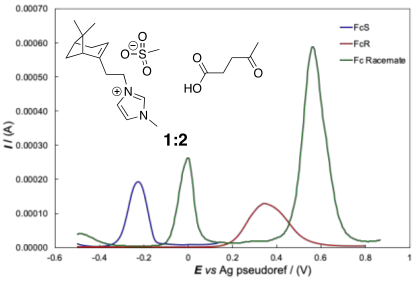

Fig. 1. Enantioselectivity tests on screen printed electrode using as additive the CDES with levulinic acid

and as chiral probe a ferrocenylic one, as pure enantiomer or as racemate

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New Families of Inherently Chiral Monomers with Different Atropisomeric Cores for Applications as Oligomeric Films in Chiral Electrochemistry

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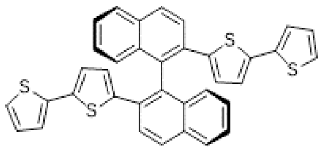
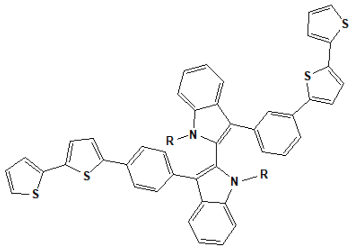
Enantioselective electroanalysis is a very attractive target, potentially enabling to discriminate between the enantiomers of electroactive chiral probes without preliminary separation steps. Inherently chiral electroactive monomers based on atropisomeric biheteroaromatic cores and oligothiophene wings have recently proved excellent starting materials for the electrodeposition of electrode surfaces consisting of inherently chiral oligomers, of outstanding enantiodiscrimination ability for chiral electroactive probes, in terms of large potential differences in voltammetry experiments [1-2]. In this context, we would like to present new inherently chiral monomers that have different atropisomeric properties and cores:

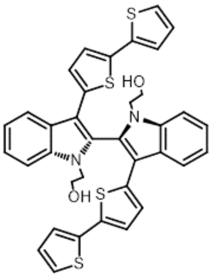
i) the new inherently chiral monomer **$Naph_2T_4$**, based on a biaromatic atropisomeric core, and advantageously obtainable in enantiopure form without HPLC separation steps, by a synthetic route hinging on enantiopure 2,2'-dibromo-1,1'-binaphthalenes;
ii) an inherently chiral monomer based on a 2,2′-biindole core **(N-R)-$Ind_2Ph_2T_4$**, as the prototype of a new inherently chiral monomer family, whose properties could be modulable through functionalization of the pyrrolic N atoms (with alkyl chains of different lengths);
iii) an inherently chiral monomer based on a 2,2′-biindole core with the N atom functionalized with an alcoholic residue **(N-OH)-$Ind_2Ph_2T_4$**



(*R*)-$Naph_2T_4$



Compound	R
(N-Me)-$Ind_2Ph_2T_4$	Me
(N-Pr)-$Ind_2Ph_2T_4$	n-Pr
(N-Hex)-$Ind_2Ph_2T_4$	n-Hex



(*R*)-(N-OH)-$Ind_2Ph_2T_4$

The monomers were electrochemically characterized by cyclic voltammety experiments, the electrooligomerization conditions were then optimized to convert the monomers into oligomeric films. The films show good stability upon subsequent potential cycling in monomer-free solution, as required for use as an enantioselective electrode surface and subsequently their enantioselection capabilities were tested using the model chiral probe *N,N*-dimethyl-1-ferrocenylethylamine, which can be regarded as a benchmark given that it displays an electrochemically and chemically reversible oxidation, but also probes of pharmaceutical interest (such as L- and D- DOPA and L- and D-Tryptophan). We have verified the general validity of the inherently chiral concept, which does not depend on the chemical nature of the atropisomeric scaffold, by testing the electro-oligomerized chiral surfaces starting from monomers with different molecular design. In order to fully clarify the enantioselection capacity of all these heteroaromatic systems, we also propose a comparison of these new inherently chiral surfaces with the benchmark monomer BT_2T_4.

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In situ Fluorescence Confocal Microscopy: a New Insight in the Reactivity of Enzymatic Electrodes

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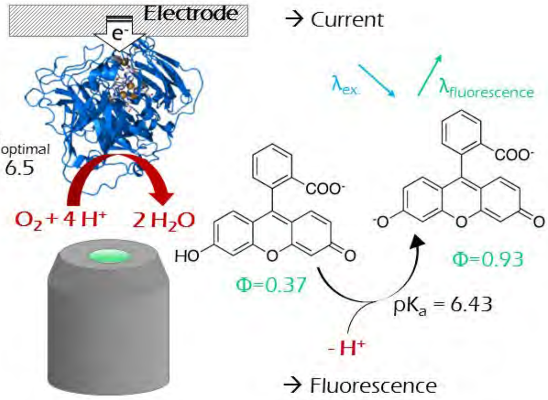
Redox enzymes, which catalyze electron transfer reactions involved in several metabolisms, are key biomolecules in biotechnological and especially bioelectrochemical devices. Thanks to unique properties, such as huge specificity and affinity towards their substrate, high catalytic turnover, and low overvoltages with respect to their substrate, they are attractive receptors in biosensors or catalysts in biofuel cells. Electrochemistry provides key information about the thermodynamic and kinetic properties of the enzymes, as well as their physicochemical behavior upon immobilization at the electrode interface. It also enables characterizing the whole biodevices. However, several information are still missing in pure electrochemical studies. Among them, spatially-resolved information are lacking since the signal is collected and integrated over the whole electroactive surface where electron transfer reactions occur. No data about heterogeneities, or local enzyme environment during turnover, are provided. In this context, the interest in coupling electrochemical methods to microscopy techniques is increasing [1]. Indeed, it enables collecting simultaneously data at the global and local scales. Among these techniques, fluorescence confocal microscopy (FCM) is a method of choice for the study of bio-objects. Moreover, it enables rebuilding three dimensional images thanks to a non-invasive optical sectioning of volumes. FCM was already implemented *in situ* during electrochemical experiments in the abiotic context. It allowed notably elucidating reaction mechanisms through the determination of concentration profiles in the diffusion layer [2]. We show here that it also permits to characterize electro-enzymatic catalysis. We chose as a model enzymatic reaction the four electron-four proton O_2 reduction in water by the multi-copper enzyme bilirubin oxidase from *Myrothecium verrucaria* (*Mv*BOD). We demonstrate that the enzymatically generated local pH changes can be visualized using a pH-sensitive fluorophore, when *Mv*BOD is immobilized at a macro- or a micro-electrode. Reactivity at the electrode surface and in the electrolyte volume can thus be explored in a new way. We observe unexpected features, especially the pH evolution of the enzyme environment, which is also indicated by a characteristic concentration profile within the diffusion layer. Finally, we obtain a cartography of the reactivity at the enzymatic electrode, which could not be determined by pure electrochemical techniques [3].

Illustration of the experimental strategy. *Mv*BOD is immobilized at an electrode which provides the electrons for the enzymatic O_2-reduction. Simultaneously, protons consumption changes the pH locally, thus modulating the fluorescence of fluorescein whose quantum yield (Φ) is pH-dependent. The evolution of fluorescence intensity is recorded through the objective by FCM. Reproduced from [3].



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Reactive oxygen species formation at Pt nanoparticles revisited by electron paramagnetic resonance and electrochemical analysis

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In the search for clean energy conversion systems, PEM fuel cells have attracted a lot of attention over the last decades. Nanostructured electrocatalysts such as porous platinum nanoparticles (NPs) are considered one of the most promising advances to lower the cost of these fuel cells and make them more commercially attractive. The efficiency of these catalysts is limited by their activity towards the oxygen reduction reaction (ORR), and most research is thus focused on understanding reaction mechanisms and improving the activity. It has been shown indirectly[1,2] that radical intermediates formed during the reaction can desorb from the catalyst surface. More importantly, these free radicals are suspected to be responsible for the degradation of the carbon support, leading to the deactivation of the electrocatalyst NPs[3].

We propose a combined electrochemical and electron paramagnetic resonance (EPR) procedure for the study of ORR intermediates generated at Pt NPs. Using spin-trap EPR spectroscopy complemented by electrochemical analysis, we show that we can detect and identify the free radicals that are produced during the ORR and are otherwise difficult to detect. Custom-made glassy carbon RDE's with a large geometrical surface area have been designed and were loaded with Pt nanoparticles via double pulse electrodeposition. The large surface area is necessary in order to produce sufficiently large amounts of free radicals to be detectable in the EPR spectrometer.

Our experiments show that only free •OH radicals are trapped by DMPO. Experiments with DEPMPO as spin trap confirm that no free •OOH radicals are present in solution. This is of great interest for on-going research to elucidate the ORR mechanism and to prevent degradation of the support and Pt electrocatalyst. We propose that our procedure can be used for a more rigorous quantification of free radicals involved in electrochemical reactions.

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Effect of Cation Solvation State of FSI-based Salt on Electric Double-layer Capacitance Performance

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The electric double layer capacitor (EDLC) is an electricity storage device that charges and discharges by electrostatically adsorbing and desorbing ions in an electrolytic solution. Since it has a long cycle life of 10^5 times or more and high output power, it has been attracting attention in recent years for memory backup of mobile devices, compensation of instantaneous voltage drop in an emergency, energy regeneration of hybrid vehicles, etc. A typical problem, however, is that the energy density is lower than that of lithium-ion secondary batteries. Since the energy density of EDLC is proportional to the square of capacitance C and the operating voltage V, expanding V is the most effective method for increasing energy density. On the other hand, C is proportional to the electrode surface area S, and the reciprocal of the thickness of the electric double layer, and so C can be enhanced mainly by increasing surface area of active material, that is, activated carbon. It is thought that pore structure optimization may have reached a limit because of difficulty in how finely the pores enhancing C can be created; hence the number of studies aiming at the expansion of C is decreasing.

Therefore, in this study, we tried to enhance C from the viewpoint of reducing the double layer thickness d. Currently, ionic species with relatively large size and low charge density are generally used as charge carriers in non-aqueous EDLCs. This is because ions with small size and high charge density interact strongly with solvents and behave as giant solvated ions, increasing d. However, in our previous research, lithium bis(fluorosulfonyl)imide (LiFSI) was sufficiently dissociated even in a low dielectric constant solvent due to small interaction with ions, and lithium ion was easily de-solvated despite its high charge density.[1,2] In this study, we succeeded in utilizing weakly solvated alkali metal cations as charge carriers for EDLC by using a mixed solvent mainly composed of low dielectric constant solvent. In addition, we will report the detailed electrochemical results of the behavior of the electrode / electrolyte interface, and also report various studies conducted to improve the usability as a device.

A composite electrode using activated carbon as the active material, acetylene black (AB) as the conductive additive, carboxymethylcellulose (CMC) as the dispersant, and styrene-butadiene rubber (SBR) as the binder was prepared and used for evaluation. LiFSI or NaFSI were dissolved at a concentration of 1.0 mol dm^{-3} in an electrolytic solution in which a high dielectric constant solvent PC and a low dielectric constant solvent DMC were mixed at a volume ratio of 1: 9 or 1: 1. A three-electrode cell was constructed using the above-mentioned activated carbon electrode for both the negative electrode and the positive electrode and metallic lithium for the reference electrode. In this study, we designed the cell so that the Li^+ adsorption / desorption behavior at the negative electrode side would be the dominant cell property. That is, the cell design was performed so that the weight of the activated carbon at the positive electrode was largely increased to reduce the influence of the positive electrode.

CV measurements carried out for 1: 9 and 1: 1 systems using LiFSI (or KFSI afterwards). In a typical electric double layer behavior, the CV curve shows a clean rectangle, but our studies showed that the rectangle collapsed during Li^+ desorption in the 1: 1 system, but hardly collapsed in the 1: 9 system. On the other hand, when the same CV was performed using KFSI, the response current for cation adsorption / desorption increased regardless of the solvent composition, Furthermore, no significant distortion was observed on the desorption side observed in the 1: 1 system when LiFSI was used. Raman spectroscopy showed that when LiFSI is used, the solvation number of PC to Li^+ in 1: 1 is much higher than in the 1: 9 system. On the other hand, as for KFSI, the solvation number of PC was about the same as that of the 1: 9 system even in the 1: 1 system. Therefore, it is considered that the difference in CV behavior is due to the difference in the solvation state between Li^+ and K^+ even in the electrolyte solutions with the same solvent composition. These results demonstrate that the use of K^+, which has a relatively low charge density, reduces the adverse effects of solvation as compared to the Li^+ system.

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Electrochemical Impedance Spectroscopy for the Characterization of Conductive Polymer Films – The Non-stationary Case

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According to the usual interpretation of the concept of impedance, impedance is not defined as time-dependent and, therefore, there should not exist an impedance out of stationary conditions. This means that if the requirement of stationarity in impedance spectroscopy is in conflict with the essential properties of the object, the measured data points are not "impedances", the obtained sets of experimental data are not "impedance spectra" and they cannot be used in any analysis based on traditional impedance models. When data recording occurs at low frequencies a complete measurement sequence can take considerable time (at least several minutes).

Many electrochemical systems, including polymer modified electrodes are intrinsically nonstationary and are affected by time-dependent phenomena. On the other hand, it is possible to show that under some suitable conditions time dependence can be conciliated into the concept of impedance [1,2]. The four-dimensional analysis (FDA) method is based on the assumption of the continuum of the object's state and parameters space. Every measured data at a given frequency should additionally contain the time of measurement (Fig. 1, a). By taking advantage of the continuity of the evolution, interpolation is performed resulting in instantaneous projections of the full impedance-time space (Fig. 1, b,c) and "reconstructed" impedances related to a selected instant of the time (Fig. 1,d). Each of these diagrams can be regarded as a stationary one, free of non-steady-state errors.

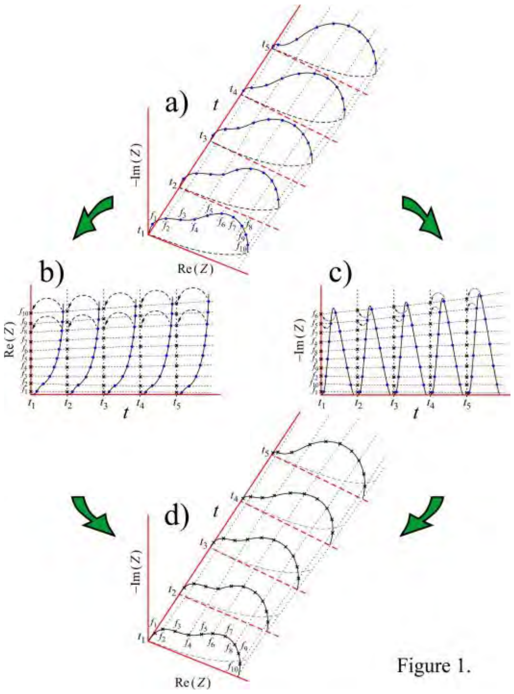

Figure 1.

Overoxidized poly (3,4-ethylenedioxytiophene (PEDOT) film on gold or glassy carbon in aqueous sulfuric acid is a good example of a nonstationary conductive polymer system for which the 4-dimensional analysis method can be effectively applied. After overoxidation, at both high and medium frequencies the complex-plane plot of the measured data is characterized by a "capacitive" arc (or depressed semicircle), while the low frequency part indicates "capacitive" behavior. However, the complex plane plots clearly indicate that the system is nonstationary [2]. E.g. it can be inferred from the shapes of the sequentially recorded impedance spectra that the charge transfer resistance at the substrate/polymer film interface decreases continuously over several hours. The impedance analysis results show that the FDA method can not only be used for the correction of the existing (experimentally measured) impedance data, but it opens up the possibility of the estimation of the impedance spectra outside the time interval of the impedance measurements.

In this study, the advantages and limitations/drawbacks of the method and its relation to CNLS-fitting are discussed.

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Structural Dependence of Capacitive Performances of Multi-Metal Oxides Composites of Ordered Support–Layer Microstructure

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An important aspect of the contemporary investigation of powdered metal oxides as electrochemical supecapacitors relates to fully precise tailoring of their synthesis to reach ordered structures of complete availability of capacitive performances. Ordered structure aims to minimize the amount of noble metal oxides, *e.g.*, RuO_2, or to improve their activity in multicomponent composites of developed interactivity between layered noble metal oxide and poorly active or inert support. The ordering is to be gained at micro- and nano-level, with structural uniformity of supporting matrices and a layer of active component(s), and consequently of composite support–layer ordered microstructural fragments. This requires intrinsic synthesis routes of an *ex-situ* or semi-*ex-situ* approach – separate synthesis of the components and subsequent impregnation, or alternatively *in-situ*, by time-programmed hydrolysis or hydrolysis within emulsified micro-reactors.

Simple *in-situ* and *ex-situ* approaches for the synthesis of powdered RuO_2-based supercapacitive composites, with TiO_2 ($RuO_2|TiO_2$) [1] and perovskite-type $LaSrCo_3$ ($RuO_2/LaSrCo_3$) [2], respectively, as supports are presented and discussed. A synthesis procedure of ultrasonically induced combined hydrothermal/aerosol pyrolysis was found suitable to produce almost ideal microspheres with surface layer of uniformly dispersed active component. Capacitive performances, investigated by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge experiments, are found sensitive to structure/composition of $RuO_2|TiO_2$, and indicated mutual improvement of the capacitive characteristics of Co_3O_4 and RuO_2 in $RuO_2/LaSrCo_3$.

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Azulene Azotetrazoles Modified Electrodes for Heavy Metal Ions Detection

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The paper relates the electrochemical characterization by cyclic voltammetry, pulse-differential voltammetry and rotating disk electrode voltammetry of new azulene azotetrazole monomers (Fig. 1). These monomers have been synthesized [1] and used to obtain modified electrodes by electrochemical polymerization. The study led to the finding conditions for the application of these complexing modified electrodes in recognition of heavy metal ions.

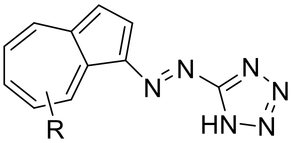

Fig.1. Investigated azulene azotetrazole derivatives; R: H; 4,6,8-Me3; 3,8-Me2-5-iPr

The modified electrodes were characterized by cyclic voltammetry in ferrocene solutions, EIS, SEM, AFM. The complexing properties of this polyfunctional material were used for the recognition of heavy metal ions (Pb, Cd, Hg, Cu) by anodic pre-concentration technique [2]. The best results have been obtained for Pb detection.

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Electrochemical Reduction of Polyacylgermanes

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Diacylgermanes such as Ivocerin® are used for dental applications as serving as non-toxic photoinitiators for radical polymerization. The corresponding photo-induced reaction mechanisms are well established [1].

Irradiation with light in the visible region leads to a homolytic C-Ge bond cleavage resulting in radical formation. The absorption spectra of the photoinitiators depend on the electron donating/withdrawing character of substituents at the aromatic moieties [2-3].

Push-pull effects, however, also indicate a substantial effect on the redox properties of the acylgermanes monitored by means of electrochemical methods. The first electron reduction of the parent compounds yields an anion radical.

In this context, we present our results obtained by DC-polarography and cyclic voltammetry across a series of mono-, di-, tri- and tetraacylgermanes, di- and tri-nuclear polyacylgermanes as well as analogical silanes and stannanes, respectively [4]. The observed trends in their first reduction potentials will be discussed connected with the substitution pattern at the central atom.

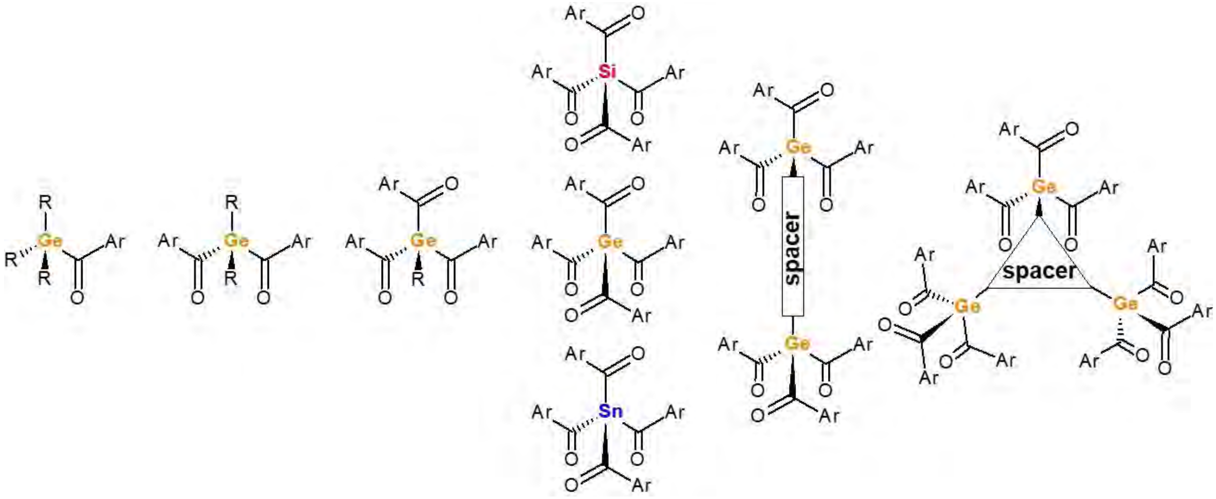

Fig.: Structures of investigated compound classes (Ar=aryl, R=alkyl).

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Enhanced Singlet Oxygen-based Photoelectrochemical Detection of Rifampicin Based on its Interaction with the Supporting Material

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Rifampicin (RIF) is an essential antibiotic for the short-course anti-tuberculosis treatment [1]. The intensive use of antibiotics including RIF results in the continuous release of the drugs into the environment, which leads to the development of antibiotic resistance genes (ARGs) and antibiotic resistant bacteria (ARB) making the treatment of some infections impossible [2]. One of the main anthropogenic sources for ARGs and ARB are suspected to be the effluents from urban wastewater treatment plants.

Therefore, there is a necessity to estimate RIF levels in biological, pharmaceutical and environmental samples. Accordingly, several analytical techniques based on chromatographic methods (liquid chromatography, thin-layer chromatography), electrochemical methods and spectrophotometry have been reported for RIF detection [1].

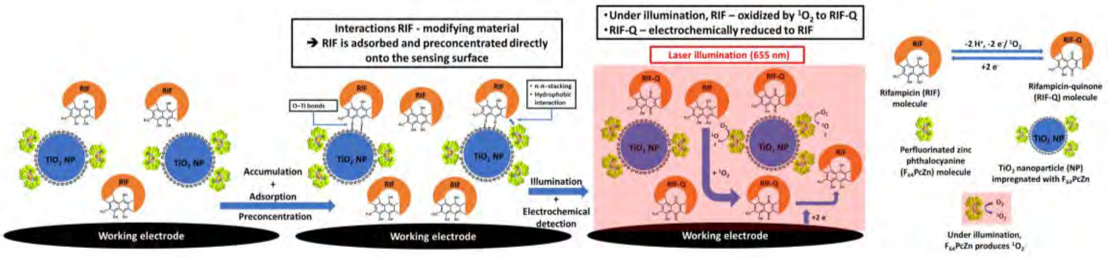

Figure 1. Schematic representation of the analytical method.

Here, we propose a new robust and sensitive photoelectrochemical method for RIF detection based on a concept developed earlier [3] using a perfluorinated zinc phthalocyanine ($F_{64}PcZn$) as a type II photosensitizer. Deposited on an electrode, $F_{64}PcZn$ generates reactive singlet oxygen ($^1O_2$) under visible light illumination resulting in oxidation of phenolic analytes. This is followed by electrochemical reduction of the product and corresponding current rise [3] in the electrocatalytic cycle similar to enzymatic sensors.

$F_{64}PcZn$ is deposited on the electrode together with a supporting element – TiO_2. The later can bring an analytical advantage due to enhanced interaction between TiO_2 surface and vicinal phenols (1,2-dihydroxybenzene, 1,8-dihydroxynaphthalene) like in the structure of RIF [3, 4]. The photosensitizer itself can also interact with RIF, both being highly hydrophobic molecules, further increasing the possibility for enhancing the overall sensitivity by pre-concentrating RIF on the sensing surface.

Using this concept and employing an incubation step, a low limit of detection of 10 nM was obtained. Also, based on the characteristics of the interaction between RIF and the sensing material, the capability of the method to distinguish from RIF and certain other phenolic compounds was also demonstrated, by testing other phenols and real samples, represented by effluents from urban wastewater treatment plants.

This approach could be even further extended for other polyphenolic compounds, based on the promising results showed.

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High-speed spectroelectrochemistry with quantum cascade laser frequency comb spectroscopy

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Frequency comb spectroscopy is a promising development, allowing for higher resolutions, faster acquisitions, and higher throughput, especially when compared with non-laser based spectroscopic techniques.[1] We have developed a spectrometer based on quantum cascade lasers, combining many advantages of dual comb spectroscopy with the relative affordability and ease of use of semiconductor lasers.

The method of dual-comb spectroscopy employs broadband lasers emitting hundreds of wavelengths simultaneously, enabling studies of the time evolution of multiple molecular absorption features. The recent advent of quantum cascade laser based mid-infrared frequency combs and the demonstration of their suitability for dual-comb spectroscopy led to the integration of the technique into a spectrometer.[2,3] This spectrometer is based on two quantum cascade laser frequency comb sources that are overlaid to produce a heterodyne beating signal.

As the spectrometer contains no moving parts, a careful selection of the mode spacings allows for spectra to be acquired on a sub-microsecond timescale, and this can be done continuously for hundreds of milliseconds. The bright laser sources allow a combination of low noise (1 mOD at 100 µs) with high spectral resolution (< 0.0001 cm^{-1}) to be achieved. Additionally, optically dense samples can be probed, for example affording measurements through highly absorbing water backgrounds. Validation of the method was done by comparing time-resolved dual comb spectroscopy measurements of a protein photocycle to an equivalent step-scan FTIR experiment.[4] Closely matching spectral and kinetic behavior was found. Furthermore, the Stark tuning rate of fluorobenzene was measured in a vibrational Stark spectroscopy experiment using the frequency comb spectrometer.[5] Most recently, the measurement of the potential dependent desorption of a monolayer of a pyridine derivative with time resolution as high as 4 µs was achieved.[6] In this presentation, we will detail the route towards in-situ spectroelectrochemical analysis with frequency comb sources and we will lay out the potential of studying microsecond dynamics in electrochemical systems.

In conclusion, the development of a solid-state mid-infrared dual-comb spectrometer based on quantum cascade lasers is detailed. Reference experiments show good signal to noise ratios at short integration times and in single-shot measurements, allowing for new applications to be explored.

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Identification of lateral water diffusion in organic coatings using time-resolved instantaneous electrochemical impedance spectroscopy

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To protect metal constructions from corrosion, organic coatings are widely applied. However, these coatings can be prone to breakdown when exposed to aqueous environments during prolonged periods of time. The initial step of failure of a coating when it comes into contact with water is water uptake. This water uptake has been studied extensively in literature [1, 2] by Electrochemical Impedance Spectroscopy (EIS) and/or gravimetry. With EIS, the coating capacitance is followed as a function of time, and the dielectric constant of the coating over time is extracted. The water uptake can then be estimated by either using the Brasher-Kingsbury equation [2] or the linear relationship [3]. This method to determine water uptake from EIS results, takes as an assumption that water only diffuses perpendicular to the surface, while lateral diffusion could also occur from a theoretical standpoint.

In this work, the validity of this assumption is investigated, by not only measuring the capacitance change of the coating surface exposed to electrolyte, but also at surfaces that are not directly exposed. The capacitance will be monitored through odd random phase electrochemical impedance spectroscopy (ORP-EIS). The test will be performed on model coatings, which are based on acrylic and/or methacrylic backbones. From initial research, it is found that the water uptake in these coatings has to be measured immediately after the immersion of the coating as it is a very fast process. This rapid water uptake in the coatings is monitored using the time-resolved instantaneous impedance calculation [4] from ORP-EIS measurements. To identify the lateral diffusion, the impedance is measured simultaneously at the immersed surface and at a surface that is not in direct contact with the solution. This measurement is performed using a custom-made dual potentiostat that shares the working electrode, which is the metal substrate underneath the coating. Results show that there is indeed a measurable capacitance increase in the measured surface outside of the immersed surface, indicating the lateral diffusion of water. The lateral diffusion coefficient can be calculated and compared to the perpendicular diffusion coefficient.

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Digital Twin of the Manufacturing Process of Rechargeable Batteries: the ARTISTIC Project

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In this lecture I report recent research progress achieved in our ERC-funded ARTISTIC project,[1] which aims at developing a digital twin of the manufacturing process of Lithium Ion Batteries (LIBs) to accelerate their optimization.[2] Such digital twin is supported on a hybrid approach encompassing a physics-based multiscale modeling workflow, Artificial Intelligence (A.I.) informatic algorithms and systematic experimental characterizations. Different steps along the battery cells manufacturing process are simulated, such as the electrode slurry, coating, drying,[3-6] calendering[7] and electrolyte filling. The multiscale modeling workflow couples Coarse Grained Molecular Dynamics, Discrete Element Method and Lattice Boltzmann simulations and it allows predicting the impact of the process parameters on the final electrode mesostructure. The predicted electrode mesostructures are injected in a 4D-resolved performance simulator capturing the influence of the pores networks and spatial location of carbon-binder within the electrodes on the electrochemical response.[3,5-8] Systematic experiments allow models validation. A.I. is used as a complementary tool to discover manufacturing parameters interdependencies directly from the experimental data,[9] to support the physical models' parameterization[4] and as a guideline for reverse engineering. The predictive capabilities of this digital twin are illustrated with results for different NMC-based and graphite-based formulations. Finally, practical implications of ARTISTIC towards the acceleration of the manufacturing process optimization of advanced batteries are discussed.

(1) ERC Consolidator Project ARTISTIC (Advanced and Reusable Theory for the In Silico-optimization of composite electrode fabrication processes for rechargeable battery Technologies with Innovative Chemistries), grant agreement #772873 (https://www.u-picardie.fr/erc-artistic/**)**.
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Experimental Evidence of the Role of Short-Range Order on the Electrochemical Activity of Iridium Oxide

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It is well known that amorphous iridium oxide materials (electrochemically synthesized or thermally obtained at low temperature) are more active than their well-crystalline counterparts, but usually it is at the expense of their stability. The presence of Ir hydroxo groups at the surface of highly active catalysts has been established.[1, 2] However, despite extensive studies, the reason of the higher activity of amorphous materials is also still the matter of a strong debate. We have recently extended the aerosol synthesis route to the preparation of highly porous noble-metals and noble-metal alloys[3] and noble-metal pure and mixed oxides.[4] In the case of pure iridium oxide, we have shown that the surface state, the crystallization and crystallite size and therefore the electrochemical properties can easily be tuned by changing the post-synthesis thermal treatment.[4] In this work, we are taking the advantage of the versatility of this green, cheap and scalable synthesis technique to prepare a large panel of iridium-non-noble metal mixed oxides. By introducing molybdenum along with iridium into the structure, we are able to delay the crystallization of the materials while the chemical transformation occurs in the same temperature range as for pure iridium. Measurements of the electrochemical activity towards the OER also show that, if the calcination temperature of the material is optimized, the activity of the catalyst is independent of the Mo content (Fig. 1).
This uniqueness allows us to decouple the influence of the oxidation state from the structure of the material and provide unambiguous proof of the impact of the interatomic ordering onto the electrochemical activity of iridium based materials towards the OER. These findings are supported by a large set of techniques including SEM, XRD, XRF and STEM-EDX (Fig. 1) as well as surface (XPS) and bulk (XAS) characterizations. Besides, to the best of our knowledge, we report for the first time the synthesis of true iridium-molybdenum mixed-oxides. Indeed, the preparation of the material by the aerosol technique permit the quenching of the initial precursor solution and therefore an intimate mixing of the two metals during the drying-step; after calcination mixed oxide $Ir_xMo_{1-x}O_2$ with $1 \leq x \leq 0.5$ can be obtained.

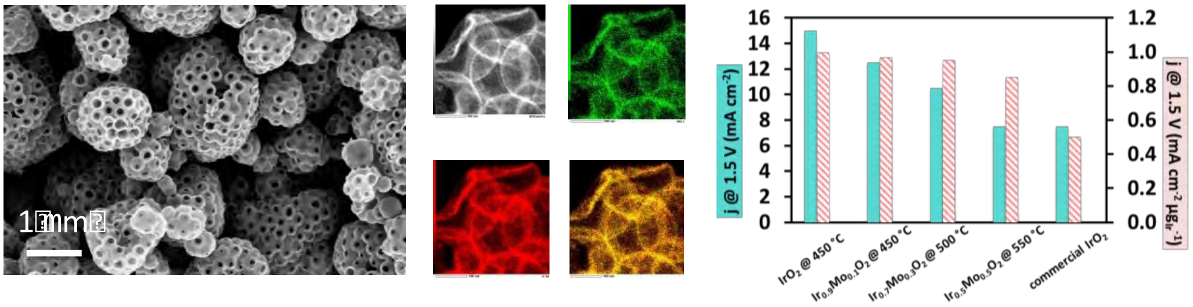

Figure 1: from left to right, SEM images of $Ir_{0.7}Mo_{0.3}O_2$ calcined at 550 °C, STEM-EDX analysis of $Ir_{0.7}Mo_{0.3}O_2$ calcined at 550 °C and histogram of activity at 1.5 V for different composition of mixed oxide refer to IrO_2

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Electrochemical Zinc Deposition onto Au(111) and Au(100) from [MPPI][TFSI]

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Zinc deposition and dissolution was thoroughly investigated in recent years for the improvement of rechargeable zinc/air batteries.[1,2] Mainly the influence of water, air and other additives on the structure of the Zn deposit and possible dendrite formation was studied.[3,4] However, the influence of the crystallographic orientation of the underlying substrate on the initial stages of Zn deposition and the structure of the Zn deposit was not focused on in detail, yet.

In this work, the differences between the electrochemical deposition and dissolution of zinc on Au(111) and Au(100) model electrodes from the ionic liquid (IL) *N*-methyl-*N*-propyl-piperidinium (MPPI) bis(trifluoromethanesulfonyl)imide (TFSI) was investigated. The aim of our study was to evaluate the role of the electrode surface structure on a possible dendrite formation

To better understand the fundamental processes which take place during the deposition and dissolution of zinc from this ionic liquid, a first characterization of the system was conducted using cyclic voltammetry (CV) and *in-situ* scanning tunneling microscopy (STM). The clearly different structures of deposits during the initial stages of zinc electro-crystallization on both gold electrodes reveal the strong influence of the crystallographic orientation on the metal deposition of zinc (Figure 1). The deposition of Zn leads to a positive shift in the cathodic decomposition potential of [MPPI][TFSI], which limits the potential window for Zn electro-crystallization.

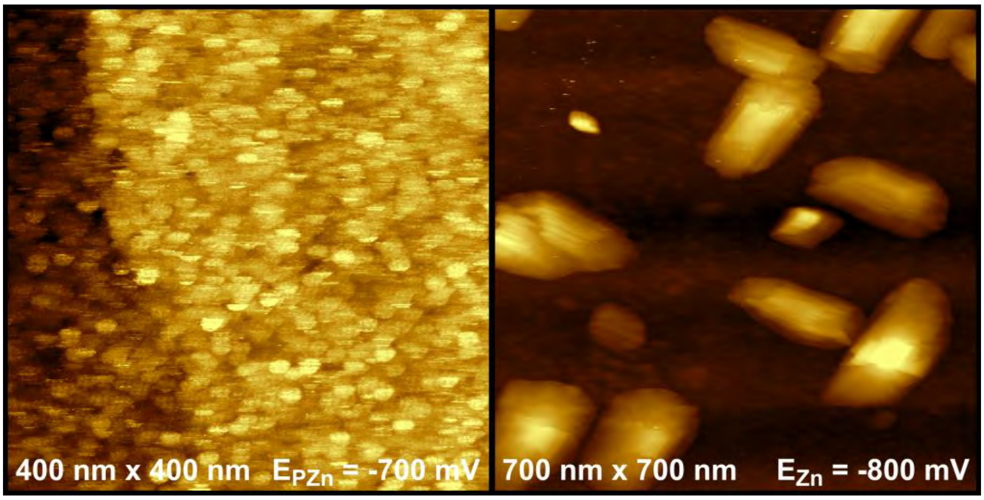

Figure 1: *In-situ* STM images of the early stages of the zinc bulk deposition on Au(111) (left) and Au(100) (right).

Zn deposits fabricated by several potential cycles were examined by Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). While *in-situ* STM as well as AES sputter experiments indicate an alloy formation that takes place during the zinc deposition a complete plating of the Au electrodes upon continued potential cycling was found. Furthermore, under the studied conditions there were no signs of dendrite formation during Zn deposition on both Au single crystal electrodes.

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Electrochemically Activated Stereoselective Functionalization of Amino Acids in Ni(II) Coordination Environment

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Elaboration of new stereoselective synthetic approaches is a topical problem nowadays since a configuration of stereocenters is often determinant in practically important properties of a compound. Novel approach based on a combination of electrochemical activation with a stereoselective synthesis in a redox active metal coordination environment opens new horizons in stereoselective functionalization of amino acids in the form of the Ni-Schiff base complexes. The approach is compatible with the modern sustainable science requirements and allows reactivity and selectivity control on the substrates at the molecular level (due to cathodic or anodic activation) thus broadening a scope of available reaction routes (including processes which were not possible in common reaction conditions).

Various types of electrochemical activation will be discussed in the presentation, including electrochemical *in situ* generation of the active species; deprotonation of the substrates using electrogenerated base, targeted regioselective activation of the different sites of the molecule, etc.
Electrochemical formation of chiral nucleophilic equivalent of glycine which is *in situ* involved in various reactions, including multistep one-pot transformations (oxy- and thioalkylation, nucleophilic addition to activated C=C and C=O double bonds, radical reactions, etc.) allowed developing practical and highly efficient electrochemical routes to various types of enantiomerically pure α-amino acid derivatives.

Mechanistic insight into electrochemical processes helpful for understanding the manner of the stereocontrol of the reactions will be provided.

Using the electrochemical approach, a number of unique amino acids in the form of Schiff bases were synthesized. Among them, novel fulleroamino acid derivatives with “double” chirality, in which amino acid is directly linked to the cage via the chiral α-amino acid carbon center providing noninherently chiral functionalization pattern; novel types of the α,α-cyclopropanated amino acids and other interesting structures will be considered.

Electrochemical functionalization made available the wide range of diastereomeric couples; each diasteromer was isolated in the individual form. This allowed performing a comparative voltammetric research on the redox properties of a series new diastereomeric Ni-Schiff-base complexes. It revealed an interesting phenomenon of the stereodependent redox activity inherent to the derivatives of various types of amino acids. The difference in the redox potential values for the diastereomeric complexes is rather significant, opening the route for the electrochemical discrimination of the stereoisomers. The origin of the phenomenon, clarified using voltammetry data and DFT calculations, will be also discussed in the presentation.

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Corrosion testing and electrochemical measurement under variable pH: experimental setup and examples of applications

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A novel experimental setup to control the pH of a sodium chloride solution during corrosion testing and electrochemical measurements is presented. The setup comprises a purpose built electrochemical cell that is separated in two compartments by a porous material which allows ions exchange. In each of the two compartments a graphite electrode is placed and connected to a computer controlled, variable voltage, power supply. A pH electrode is immersed into one of the two compartment (the test compartment) and connected to a controller which sends the pH value to the computer. In the same compartment where the pH electrode is placed, an independent counter electrode, an Ag/AgCl reference electrode and a working electrode (i.e. the material under study) are placed. An automatic controller connect the two graphite electrodes placed into the two half cells and applies a sufficient potential to develop hydrogen from one electrode and oxygen from the other. As a result, the pH in the half cell where hydrogen is developed increases, whereas the pH in the half cell where oxygen develops decreases. By alternatively measuring the pH in the test cell and applying adequate potential to the graphite electrodes, it is possible to vary the test cell pH precisely and to perform pH sweep experiments. Further, the same controller enables to perform electrochemical measurements on the working electrode placed in the test cell. As a result, it is possible to obtain information on the variation of electrochemical behavior as a function of pH with a single experiment. This paper presents the experimental setup and provides some example of applications, such as that illustrated in Figure 1 below.

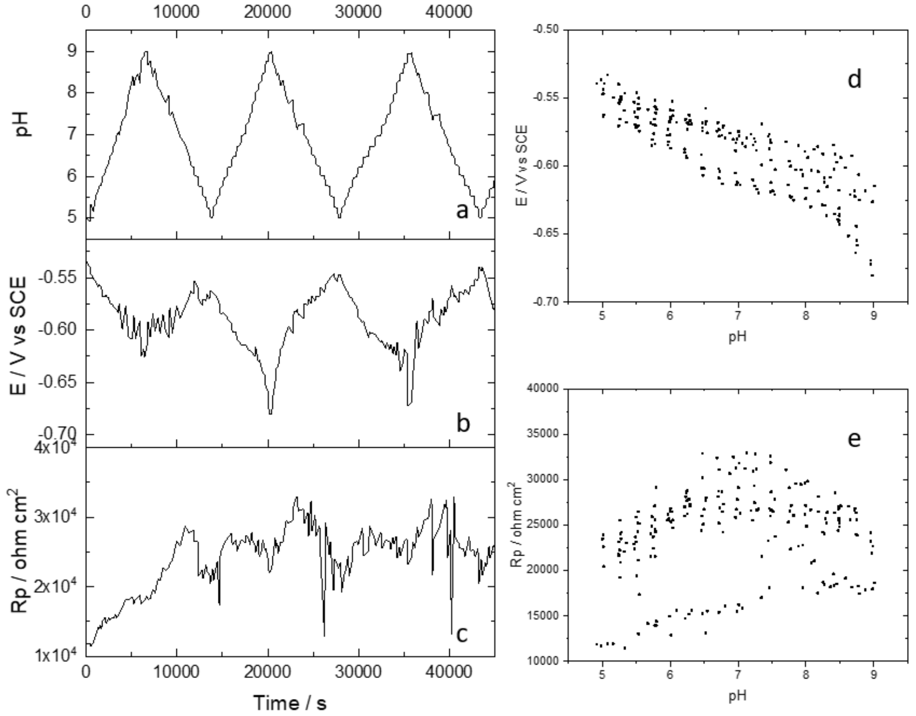

Figure 1: pH (a), corrosion potential (b) and polarization resistance (c) as a function of time for an AA2024T3 specimen immersed in 3.5 wt.% NaCl solution. For the same experiment, the corrosion potential (d) and the polarization resistance (e) as a function of the solution pH.

Influence of Micrometric Inter-electrode Distances and Water Hardness on Mineral Scaling at the Electrode Surface during Electrochemical Advanced Oxidation Process

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In electrolytic water treatment, scaling or deposit is an inevitable challenge and it normally ends up in capital loss due to technical issues. When the electrode is polarized at a sufficiently negative potential, dissolved oxygen and water are reduced to hydroxyl ions [1, 2]. These two phenomena result in an increase of local pH at the vicinity of electrode. In presence of Mg^{2+} and Ca^{2+}, hydroxide scales can potentially be produced. On another side, this pH increment also shifts the thermodynamic ratio of carbonates/bicarbonates favoring the production of carbonate scales [3-5]. Several authors have reported the formation of scaling in an electrochemical setup while working with different hard water coming from multiple sources: cooling water used in industries [9, 10], artificial underground water [11], artificial [4] and real seawater [12]. Due to abundant resources capable of restricting the application of electrolysis, meticulous study to comprehend and to avoid the formation of deposits seems primordial.

The influence of reactor design on mineral scaling was investigated in this study by considering a microfluidic thin-layer cell in micrometric range compared to electrolyzer with inter-electrodes distance in centimeter range [6, 7]. Short distances have shown to enhance mass transfer within the cell and it overcomes the barrier of working with low ionic conductivity electrolyte [8]. $Mg(OH)_2$ and $CaCO_3$ deposits were selected in this work, as they are the main scales encountered in the field. The objective was to establish optimal operating conditions of microfluidic electrochemical cell in-which the scaling does not occur for all-type of hard waters. The results present here-in are the first to report on the scaling in microfluidic thin-layer cell. Its configuration is distinct as compared to that found in the literature where rotating disk electrode was used as working electrode. In particular, its electrode surface area is 25 to 250 times bigger relatively to the rotating disk electrodes (0.2 to 2 cm^2). The electrochemical cell is hence more representative to reactors used on a larger scale.

The applicable current density range was larger with thin films in comparison to centimetric inter-electrode distances to prevent scaling formation, which could enlarge the applications of micro-reactors. Coupling the experimental results with voltammetry and impedance spectroscopy allowed depicting the mechanism of nucleation and scaling. Mathematical models were fitted to the experimental results to validate scientific approach notably on the effect of applied current density, inter-electrode distances and matrix of electrolyte.

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Recent Advances on Wearable Platforms for On-body Analysis Using Membrane-Based Sensors

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Recent investigations of wearable electrochemical sensing have largely focused on development of flexible materials and electronics using traditional electrochemical sensing principles (i.e., potentiometry and amperometry) without genuine innovation of the chemical design, interrogation and readout parts. This has limited the true digital transformation of this fascinating concept because those devices do not meet the minimum requirements for healthcare purposes, such as being calibration-free, having strict validation and correlation, robustness during on-body measurements, cytotoxicity assessment and analytical reliability, among others.[1] In this talk, recent advances that include the analytical development and evaluation of the sensing part of wearable electrochemical sensors for on-body monitoring of certain physiological parameters will be discussed. Importantly, the selected wearable devices exclusively contain membrane-based sensors and are classified in two types of platforms: (i) epidermal patches for the analysis of ions and biomolecules in sweat encompassing perspiration during sport practice; and (ii) (micro)needle-based platforms for the intradermal determination of ions and biomolecules with clinical purposes.

The engineering of epidermal patches for real time characterization of sweat has required special attention in the design and fabrication of appropriate microfluidic system allowing for the creation of a safe path or the sweat coming from the eccrine glands towards the electrodes' surfaces, with no contamination or evaporation risk while providing a passive sweat pump encompassed to the sweat rate in the individual.[2] Having achieved that, the most crucial issue is to demonstrate the analytical reliability of on-body measurements through a meticulous and reliable validation strategy. This implies the accomplishment of a protocol based on sweat sampling and its analysis using a standard analytical technique that has been recently suggested by our research group, for example ion chromatography for ions but also for glucose and lactate. Specifically, it has been demonstrated that on-body measurements in sweat involving enzyme-based sensors require for pH and T correction towards more accurate outcomes. On the other hand, of special interest is the case of lactate detection, since particular efforts are needed in the electrode design to reach the required levels expected in sweat (ca. from 1 to 25 mM). Several strategies will be inspected in the talk.

Intradermal analysis using membrane-based sensors has additional handicaps related to the biocompatibility of the tailored electrodes as well as physicochemical resistance to skin penetration. The platform used per excellence to reach the desired level of penetration is (micro)needles that are adequately modified to sense different targets. Different sizes and designs would in principle allow for the availability of interstitial fluid, blood and intramuscular measurements. However, up to date, only in vitro tests have been presented in the literature.[3, 4] In our research group, we are working in one step further in terms of validation strategy, in vitro simulation of skin penetration and field experiments in mice based on *post mortem* measurements. In particular, recent advances on the monitoring of scaffolds degradation my measuring pH and lactate by means of new (micro)needle-based devices will be presented.

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The Role of Poly(3-octylthiophene) as Redox Mediator of Ion Fluxes Across Voltammetric Thin Membranes

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Previous publications have demonstrated the effective tuning of ion-transfer processes across ion-selective membranes formulated with a thickness in the nanometer order by modulating the oxidation state of a film of poly (3-octylthiophene) –POT– that is in backside contact.[1, 2] The beauty of the concept is based on the connection of the charge transfer (CT) process occurring in the POT lattice with any ion-transfer (IT) process at the sample–membrane interface, being framed by the application of a linear sweep potential rather than the typical measurements with ion-selective membranes at zero current (i.e., traditional potentiometry). Several attempts on the theoretical description of this CT-IT system considered the Nernst equation for the description of the POT oxidation process, providing a sigmoid-shaped curve for the CT.[3, 4] Besides some theoretical assumptions, to the best of our knowledge, there is no experimental evidences confirming this behavior of the CT whether this process comes coupled to IT process(es) of different nature. In this talk, a new strategy for the experimental characterization of the CT process in POT films involved in different CT-IT systems is presented. For this purpose, we take advantage of the absorbance change in the POT film while being oxidized to monitor the CT process linked to non-assisted and assisted IT at the sample–membrane interface. Thus, spectroelectrochemistry is used as the readout of ITO-based electrodes modified with a double layer design comprising POT and the ion-selective membrane. In particular, the concept is demonstrated for membranes containing one (potassium), two (lithium and potassium), and three (lithium, sodium and potassium) ionophores, thus promoting a change in the nature and number of the IT processes.

The CT visualizes as independent sigmoid appearing at different potential ranges according to the assigned IT process. Advantageously, it is here proposed an easy calculation of both CT (dynamic absorbance versus applied potential) and IT (coulovoltagram) based on the Sigmoidal–Boltzmann model. Both experimental and theoretical definition of the role of POT as redox mediator of ion fluxes across voltammetric thin membranes open up new possibilities for the further design of sensors with superior analytical features, mainly in terms of improved selectivity because of the independency of CT according to different IT occurring in the electrode. In addition, the Sigmoidal–Boltzmann model may allow for the calculation of ion-ionophore binding constants in the membrane using an easy relationship between the peak potentials corresponding to non-assisted and assisted ITs.

In addition, the linear correlation found with the concentration of the cation(s) analyte(s) in the sample solution on the basis of the newly proposed spectroelectrochemical experiments deserves special attention towards further analytical purposes. A deep optimization of membrane thickness, scan rate in the applied linear sweep potential as well as frequency acquisition (and resolution) of the optical measurements will contribute to a fine tuning of the obtained linearity. The tandem light-electrochemistry has demonstrated a series of unique fundamental but also analytical applications that are inaccessible with other techniques: mechanistic studies, analytical electrochromic devices, protein-related investigations and analytical sensors among others. In particular, the electrodes herein developed based on nanometer-sized membranes in backside contact with POT present a high potential towards real-time extracellular measurements of different ions used to stimulate the cells in conjunction to light, undoubtedly offering new horizons in this field.

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Tuning the selectivity of CuAg core-shell nanoparticles towards CO through a combination of high-end electrochemistry and electron microscopy

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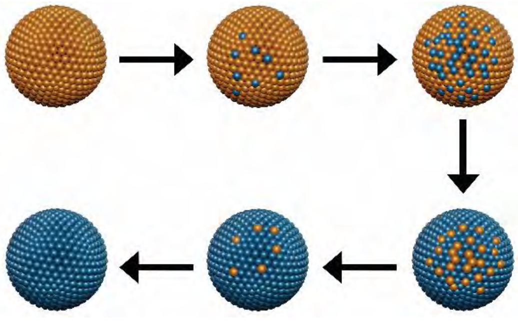
Due to the continuous combustion of fossil fuels into the atmosphere, an historical high point was reached in 2015 when CO_2 emissions exceeded the threshold of 400ppm. It is broadly known that the excessive emission of CO_2 has a negative impact on the environment. It is therefore of utmost importance that the CO_2 concentration is inhibited by reducing the combustion of CO_2 into the atmosphere in order to mitigate the effect on global warming. In this context, CO_2, as a feedstock, represents a great alternative for the synthesis of fuels and valuable chemicals. Utilizing renewable energy sources as the required energy supply to convert this CO_2 into value added products has the additional advantage that the process is CO_2 neutral. Since renewable energy displays the fastest growth of all this implies new challenges concerning production-consumption profile matching for which the electrochemical conversion of CO_2 offers a solution [1]. Electrochemical conversion of CO_2 is one of the most promising routes because of the ability to tune the product selectivity by adapting the operating potential and catalyst material [2].

In this research, CuAg core-shell nanoparticles are used as electrocatalysts to convert CO_2 in CO. As broadly known, by combining metals with certain arrangements, energetic effects lead to the ability to tune the product selectivity. In case of CuAg core-shells nanoparticles, the product selectivity is tuned towards CO because of the change in adsorption of CO_2 on the catalyst surface. By reducing the size of the CuAg core-shells, more electrochemical active surface area (EASA) is obtained using significantly less material, making the total process less expensive.

The gap in current research is the knowledge on ideal shell thickness to convert CO_2 into CO. Here, we gained novel insights into the influence of the shell thickness on the electrochemical reduction of CO_2. The CuAg core-shell nanoparticles where synthesized through a colloidal method succeeded by galvanic displacement of Ag with Cu [3]. The shell thickness was varied by using different Ag concentrations and displacement times. The activity of these electrocatalysts was firstly studied in an in-house designed H-type cell with an aqueous solution of $KHCO_3$ saturated with CO_2. The activity was screened with cyclic voltammetry to compare the onset potential of the different core-shells. Further information on the selectivity was gained by analyzing the materials in an in-house designed electrolyzer. Chrono-amperometry experiments were performed, gaseous products were analyzed with an in-line gas chromatograph (GC) and the liquid products with a HPCL. Finally the core-shell structures were investigated by TEM, to understand the link between the structure, the activity and the selectivity.



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Hydrogen Generation Derived from Water Dissociation (24)

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We created a two-compartment cell (2CC) separated by a bipolar membrane (BPM[1]) sandwiched between a through-holed (TH) electrode assembly (BPMTHEA-2CC) with the distinguishing feature of integrated functionality of dualities based on the Golden Rule for sustainable water splitting derived from water dissociation (WD) with a dual chemical bias (CB).[2,3] A decisive advantage of this system is that all electrolytes used are sustainable because the reaction starts from WD. The opposite bidirectional charge separation of H^+ and OH^- ions derived from WD generates inner CB within BPM. Many anolyte–catholyte combinations are possible in BPMTHEA-2CC, which induces outer CB (OCB). Therefore, dual CB reduces overall water electrolysis voltage. We present here supporting proof of our concept.

We have achieved hydrogen generation derived from WD with BPMTHEA-2CC using an oxygen evolving reaction active TH dimensionally stable anode (De Nora Permelec Ltd) prepared on Pt gauze. Liberated gas was analyzed using a gas chromatograph (GC-390B, GL Sciences) equipped with a stainless-1/8”x3m MS-5A 30/60 column and a thermal conductive detector (TCD). We succeeded in detecting appropriate amounts of molecular hydrogen generated in the cathodic compartment of BPMTHEA-2CC, anolyte (water)|TH anode|BPM|TH cathode|catholyte (water), by imposing a voltage with less than the theoretical 1.23 V for water splitting at room temperature.

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Probing the activity of Fe-peroxo porphyrin intermediates in reaction layer during electrochemical reductive activation of O_2

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Oxidations are an important class of reactions in the chemical industry for the production of huge quantities of intermediate and final products. In the current economic and environmental context the ideal oxidant is O_2 as it is abundant and benign. The use of Fe porphyrins (Figure 1A) is an interesting biomimetic approach for O_2 activation as Fe^{II} can reproduce the metabolic transformation catalyzed by Fe enzymes such as CytP450 [1]. The optimization and control of the O_2 activation process requires a complete understanding of the mechanism and the identification of intermediates involved. Some of these intermediates being very reactive, their lifetime are very short making them difficult to detect experimentally. Thus there is a need to develop *operando* methodologies to probe them at the earlier stage of their formation directly in reaction layers.

The scanning electrochemical microscope (SECM) is a perfect tool to capture, quantify and characterize short-lived intermediates, including in complex molecular homogeneous catalytic systems [2,3].

Herein we propose to use the SECM in generation-collection mode to quantitatively analyze O_2 reductive activation in organic media catalyzed by three different Fe porphyrins as illustrated in Figure 1. We particularly focus on the first intermediate produced in non-acidic medium, the (peroxo) intermediate $Fe^{III}(OO^{2-})$ adduct issued from the reduction of a (superoxo) $Fe^{III}(OO^{\bullet -})$ formed from the binding between O_2 and Fe^{II}).

In one single SECM experiment new thermodynamic and kinetic parameters such as the redox potential of the intermediate, the association constant of Fe^{II} with O_2 and the pKa of the $Fe^{III}(OOH^-)$/ $Fe^{III}(OO^{2-})$ couple can be obtained and related to earlier DFT calculations [4]. Such information, obtained in the absence of H^+, are then related to the efficiency of these catalysts for O_2 reduction in the presence of H^+. The results obtained can contribute to a further understanding of the parameters controlling the catalytic efficiency of the Fe porphyrin towards O_2 activation and reduction.

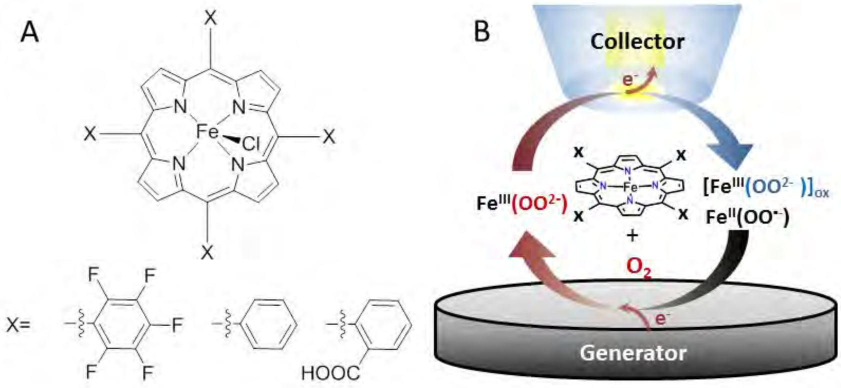

Figure 1: A) structure of the porphyrins complexes used. B) Principle of the SECM experiments

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In Situ Raman Study of Interfacial Water Structure at Pd Single-Crystal Surface

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Water molecules are essential component of the electrochemical double layer (EDL) during electrochemical reaction process. The discharge processes of water molecules or hydrated proton are the initiation of the classical hydrogen evolution reaction (HER). Thus, the structure and composition of interfacial water molecules directly affect the HER process. Pd has excellent HER performance. The study of interfacial water molecules of Pd single-crystal surface is of great significance for understanding the HER process. However, the perception of water molecules during the HER process at Pd single-crystal surface has been still elusive due to the complex interfacial environment, such as various water orientations, hydrated ions, and hydrogen bonds network in water molecules [1].

Herein, using electrochemical in situ shell-isolated nanoparticle-enhance Raman spectroscopy (SHINERS) [2] and ab initio molecular dynamics (AIMD), we systemically investigated the structure and composition of water molecules from interfacial solution phase and electrode phase during the HER process. It was found that the interfacial water is mainly composed of water of trihedrally and tetrahedrally coordinated water and Na^+ hydrated water ($Na.H_2O$) at Pd surface. The structure and composition of interfacial water dynamically changes and forms an ordered structure as HER progress. Meanwhile, we studied interfacial solution phase (ion concentration and types) for the influence of interfacial water and HER. We found that the population of $Na.H_2O$ in high concentration electrolyte is the highest in interfacial water molecules, while the HER also shows a better performance in the same condition. Thus, according to the increased population of $Na.H_2O$ in high concentration electrolyte, the ordered $Na.H_2O$ plays a key role during HER process.

To understand the role of ordered $Na.H_2O$ during HER, we further investigated the electrode phase (crystallographic orientation and electronic structure) for the influence of interfacial water and HER, Pd (111) shows the best HER performance and the highest population of $Na.H_2O$ in three low-index Pd (hkl) single-crystals. Therefore, we believe that $Na.H_2O$ is more conducive to water dissociation during HER process. The ordered interfacial water structure could accelerate the efficiency of electron transfer. Theoretical calculations also show that $Na.H_2O$ is more susceptible to dissociate HO-H bond than trihedrally and tetrahedrally coordinated water at electrode surface during HER process. We propose a new structure-relationship between the interfacial water and HER, which could help to understand the nature of electrocatalysis.

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Mapping Potential Gradient Distribution in Bipolar Systems using Electrogenerated Chemiluminescence

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Bipolar electrochemistry has gained remarkable interest in recent years as a powerful technology for the modification of conductive objects and for the electrochemical synthesis of novel functional materials in a wireless mode[1],[2]. In fact, differently to conventional electrochemistry, bipolar electrochemistry offers the extraordinary advantage to perform electrochemical reactions at both extremities of a wireless electrode, or bipolar electrode (BPE), through the application of an external electric field generated in a low concentration of a supporting electrolyte.

Bipolar systems, which are generally composed of an electrochemical cell and a pair of driving electrodes, can be designed with different geometries and configurations, in order to achieve the electrosynthesis of functional materials with desired morphologies and characteristics. For example, bipolar electrolysis using a cylindrical insulator enabled the perpendicular growth of a uniform conducting polymer array[3], or the electrochemical fluorination of triphenylmethane was performed in a U-shaped electrochemical cell employing a split BPE system[4]. Nevertheless, the distribution of potential gradient in these bipolar systems is dynamic and gradually changing and its direct monitoring is hampered due to the wireless nature of the BPE. The possibility to obtain a direct indication of the potential distribution would have tremendous impact on the application and further development of original bipolar systems.

In the present contribution, we explore the use of Electrogenerated Chemiluminescence (ECL) to visualize the distribution of potential gradient at the level of a BPE in such bipolar systems. The ECL technology represents the ideal approach due to the electrochemical nature of light emission. In fact, ECL involves the generation of photons at the electrode surface triggered by an electrochemical stimulus and, nowadays, it is widely employed as a highly sensitive imaging technique[5]. Our method exploits the use of a mixture of different chromophores in solution that, in presence of a coreactant species and upon application of anodic potentials at the BPE, can be simultaneously electro-oxidized generating mixed ECL emissions at different wavelengths. Since every luminophore is characterized by a specific oxidation potential and a typical wavelength for ECL generation, the mixed ECL emission can be resolved and associated to the correspondent single emitting species and, hence, to the correspondent oxidation potential. This approach permits to map the distribution of potential gradient in a specific bipolar cell, and can be applied to any other bipolar system in general.

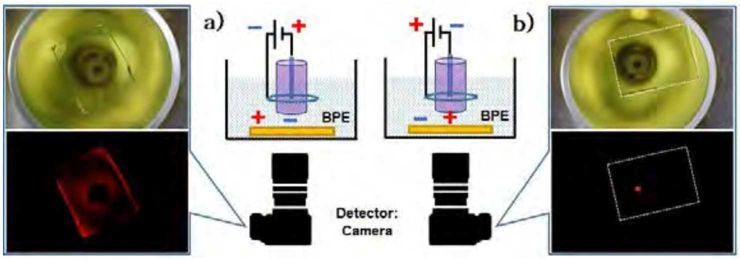

Figure 1: ECL emission of $Ru(bpy)_3(PF_6)_2$ 0.05 mM / TPrA 10 mM system in acetonitrile solution at BPE in cylinder configuration with different polarities: a) cathodic area under the cylinder and b) anodic area under the cylinder.

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Thermal Stability of Electrodeposited Ni-Mo Alloys in the Light of Detailed Structural Studies

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Alloying Ni with another highly corrosion-resistant component leading to strengthening is a field of interest in plating industry. Alloying Ni with oxoanion-forming metals such as Mo, W and Re is possible from citrate-type baths with the so-called induced codeposition mechanism. In this work, electrodeposition was performed from a solution of small citrate content (citrate/Ni^{2+} ratio: 0.5) with no volatile component (like NH_3). The concentration of Na_2MoO_4 in the bath was the varying parameter. The highest deposition efficiency, $\eta \approx 0.94$, was found for pH = 6.1, regardless of the current density applied. Both the increase in the molibdate concentration and the decrease in current density resulted in the increase of the Mo mole fraction in the deposit. Saccharine as stress reliever was found to be beneficial for the deposition of crack-free samples.

X-ray diffraction full line profile analysis was carried out to study the microstructural parameters such as the crystallite size, the dislocation density and the stacking fault probability. The increase in the Mo content up to 5.3 at.% led to one order of magnitude enhancement of the dislocation density while the crystallite size reduction was less significant. In addition, the twin boundary formation activity during deposition increased with increasing Mo concentration. The results obtained were compared with bulk nanocrystalline Ni-Mo materials with similar compositions but processed by severe plastic deformation. It was found that the microstructure in electrodeposited Ni layers is more sensitive to the Mo concentration than bulk ultrafine-grained Ni-Mo materials processed by severe plastic deformation.

Differential scanning calorimetry (DSC) experiments were performed on the Ni films deposited with and without Mo to study the thermal stability of the deposits. It was revealed that the increase of the Mo mole fraction in the deposit significantly improved the thermal stability of the nanocrystalline microstructure in Ni layers, despite the much higher defect density and smaller grain size which act as thermodynamic driving force for recovery and recrystallization. The better thermal stability can be attributed to the pinning effect of Mo solute atoms on the lattice defects (e.g., dislocations and grain boundaries) during annealing. The comparison of thermal relaxation processes of the electrodeposited samples and those obtained with severe plastic deformation (SPD) revealed that the annihilation of the structural faults takes place at the same rate as referred to the original defect density of the specific samples, although the defect densities were distinctively different for samples obtained with the two procedures.

The energy stored in the crystallographic defects in the nanocrystalline Ni-Mo alloy films was also determined from the DSC experiments. It was revealed that the majority of the heat released during DSC (~77%) was related to the grain boundaries. It was also found that the increase of Mo content from 0.4 to 5.3 at.% yielded an enhancement of the stored energy with a factor of about two. In the SPD-processed samples, there was a considerable contribution of vacancies to stored energy while their effect in the electrodeposited layers was lower.

The structural changes as a result to the increase in the Mo mole fraction to 5.3 at.% caused a fourfold increase in the yield strength for the latter sample. The Ni film with low (0.4 at.%) Mo concentration showed a normal strain hardening while the sample having high Mo content exhibited a continuous softening after a short hardening period. The strain softening was attributed to detwinning during deformation.

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Studying Water Reactivity at Electrochemical Interfaces by Nanoconfinement Strategies

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Understanding and controlling water reactivity at electrochemical interfaces is pivotal for the development of electrochemical energy storage and conversion devices such as water electrolyzers or aqueous batteries, among other systems. However, it is a rather challenging task owing to the ambivalent role played by water as both solvent and reactant, which often masks reactive water molecules at interfaces in their surroundings. Unfortunately, only few techniques can be used to determine the water structure (density, orientation etc.) in the first molecular layers at electrochemical interfaces. Among them, operando spectroscopies were employed. While powerful, they are often limited by their spatial resolution and generally require the use of model electrodes. Similarly, computational chemistry approaches prove very powerful but suffer from the large computing cost of including explicit solvent molecules as well as taking into account charge transfer.

Unlike for electrochemical systems, assessing the ability for water to interact with itself or its environment has always been pivotal to understand nature phenomena such as the folding of proteins, the winding of DNA or the complex organization of lipids into sheets. Strategies were thus developed to isolate water molecules in specific environments and study their behavior/reactivity. In this work, we demonstrate a strategy consisting in confining water molecules inside an organic liquid matrix in order to form aqueous nano-domains. Varying the concentration of water and/or supporting salt, we further demonstrate that the size of the aqueous domains can be tuned and found that the reactivity of these domains at electrified interfaces depends on their size and chemical composition. In definitive, we show that complementary to the develop of spectroscopic tools capable of probing at the nanoscale active sites and their environment, another promising complementary approach relying on the control at nanoscale of the reactant itself, e.g. water, can be taken. Doing so, strength of short- and long-range interactions can be selectively studied, which can then be used to develop more efficient and selective electrocatalysts for water, CO_2, O_2 or N_2 reduction.

Molecular-level Analysis of Catalytic Activities of Electrode Surface for Electrochemical Deposition Reactions using Theoretical Calculations and Surface Enhanced Raman Microscopy with Plasmonic Sensors

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Electrochemical deposition reactions have been widely utilized to prepare functional surfaces with controlled micro/nano structures featuring their precise controllability. In order to establish the methodology to achieve further higher performance and precise control, molecular-level understanding of the reaction mechanisms is required. For this, we attempted to apply theoretical calculation such as density functional theory (DFT) as well as surface enhanced Raman microscopy equipped with plasmonic sensors. In this work, we will describe these approaches with some of resent results. By using DFT calculations, we investigated the catalytic activity of the electrode surfaces for the reaction of reductants for electroless deposition processes, including the behavior of their intermediate species, the interaction with additive species, as well as solvation effects. While the DFT analysis provides quantitative insights for the origin of the catalytic activity of the electrode surfaces and the reaction mechanisms, obtaining these data from experimental approach is challenging. In order to overcome this, we applied surface enhanced Raman scattering (SERS) equipped with confocal microscopy and developed plasmonic sensors with controlled nanostructures to achieve very high signal enhancement. For the plasmonic sensors, we developed “reflection” type and “transmission” type sensors, which could achieve very high sensitivity analysis[1]. Furthermore multi-confocal type SERS microscopy was employed for mapping and imaging analyses of the electrode surface as well as local pH distributions. By using these techniques, various systems have been investigated and modelling of their reaction processes has been carried out.

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Surface Modification of Metal-Insulator-Semiconductor (MIS) Photoanodes with Prussian Blue Analogs

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Recently, redox-active Prussian blue analogs (PB) have gained attention to be promising water-oxidation electrocatalysts integrated with semiconductor absorbers for photoelectrochemical (PEC) water splitting, due to high catalytic activity, low cost and facile fabrication.[1-3] Especially, CoFe-Prussian blue analog (CoFePB) performs exceptional stability in acid media.[4] In previous work from our group, Si photoanodes based on the metal-insulator-semiconductor (MIS) junction were modified with NiFe-Prussian blue analog (NiFePB) by electrodissoluting homogeneous Si/SiO_x/Ni photoanode. This modification transformed homogeneous to inhomogeneous Si/SiO_x/Ni MIS junctions, and led to considerable photovoltage (V_{oc}) enhancement.[5] Furthermore, these modified Si photoanodes exhibited a pronounced electroactivity for oxygen evolution reaction (OER) and urea oxidation reaction (UOR).
In this presentation, with the aim of extending the knowledge on the photoelectrochemical properties of these inorganic systems, we introduce the modification of CoFePB and NiRu-Prussian blue analog (NiRuPB) on homogeneous Si/SiO_x/Co and Si/SiO_x/Ni MIS electrodes, respectively. CoFePB was deposited by chemically etching Co layer, meanwhile NiRuPB was introduced by electrodissolution of the Ni layer in the presence of the metal cyanide salts. The electrochemical properties of two systems were studied, which unveiled clearly-defined and distinct electrochemical responses. Interestingly, the V_{oc} of *n*-Si/SiO_x/Ni/NiRuPB were significantly improved from ~200 to >350 mV with an increasing modification time. Conversely, *n*-Si/SiO_x/Co/CoFePB ones were found to be independent on modification (~230 mV). We do think that these surprising distinct behaviors are indicative of a different morphology of the MIS junction, that was investigated by atomic force microscopy and scanning electron microscopy. Additionally, the NiRuPB-modified Si photoanode with the optimal V_{oc} was employed for solar-driven OER and UOR, exhibiting a remarked photocurrent density of 8.3 and 17.5 mA cm^{-2} at 1.23 V vs RHE, respectively. This finding demonstrates that our surface modification could bring a new strategy to develop low-cost solar hydrogen technology.

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Boron Nitride Nanosheet as Novel Electrocatalysts for Oxygen Reduction Reaction and Hydrogen Evolution Reaction
- Combination with Inert Substrates and Metal Nanoparticles -

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Electrochemical energy conversion plays central roles in the future sustainable society based on renewable energy. For example, hydrogen, one of the most important carriers, is produced by electrolysis of water and is converted back to electricity by hydrogen - oxygen fuel cell. Electrochemical hydrogen evolution reaction (HER)/oxygen evolution reaction (OER) and hydrogen oxidation reaction (HOR)/oxygen reduction reaction (ORR) are elemental processes in water electrolysis and hydrogen - oxygen fuel cell, respectively. The rates of these reactions are strongly dependent on electrode materials, i.e., electrocatalyst [1], which are the key to improve the efficiencies of electrochemical energy conversion processes.

Large overpotential for ORR is one of the most serious problems in the development of fuel cells. Although Pt group metals are the most efficient electrocatalysts, world-wide efforts have been made to find alternative catalysts because of their high cost, less abundance, poor stability, and still sluggish kinetics.

We proposed theoretically [2-5] that boron nitride, which has similar geometric structure to that of graphite but is an insulator with a wide band gap (˜5.8eV) and, therefore, is not considered as an electrocatalytic material, may act as an efficient electrocatalyst for ORR when it has defects or is placed on inert metal gold substrate such as Ni. Electrocatalytic activity for ORR of BN placed on gold substrate, which is inert for ORR with 2-electron process and high overpotential, is experimentally proved, although ORR still proceeds by 2-electron process [5, 6]. Among various types of BN, BN nanosheet (BNNS) shows highest activity. By decorating BNNS by gold nanoparticles (AuNPs: 5 ~ 30 nm), 4-electron ORR route to water is open, although only ca. 50% of oxygen is reduced to water [7]. Theoretical free energy analysis shows that 4-electron reduction becomes possible because small Au clusters drastically stabilize adsorbed O by 1.6 eV, making the dissociation of adsorbed OOH, which is an uphill process at BNNS/Au electrode, downhill. Considering the importance of BN/Au interface, one would expect further improvement of electrocatalytic activity for ORR by using smaller AuNPs for decoration. It is found that not only the overpotential is reduced further by 100-120 mV and is only 100 mV more than that at a Pt electrode but also more than 80% of oxygen is reduced to water at the Au electrode modified by BNNS decorated with AuNPs of small size (ca. 5 nm) with narrow size distribution [8].

We also found that BNNS/Au is a good electrocatalyst for HER [9]. DFT calculation suggests that the origin of small overpotential is the existence of energetically favored sites at BN edge for adsorbed hydrogen, i.e., intermediate state, and further improvement of electrocatalytic activity for HER by increasing the fraction of atoms at the edges of BNNS on Au substrate, which can be achieved by decreasing the size of each BNNS at a given amount of BNNS on the surface. Actually, it is proved that the smaller the BNNS size, the lower the HER overpotential [9]. AuNPs modification is effective for the reduction of HER overpotential [10]. Amounts of Au can be reduced by using nanoparticles of Au alloys by other metals such as Ni, Cu, and Co [10].

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Novel Non-Liquid Electrolytes for EIS Characterization of Surface Layers on Heritage and Art Objects

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Electrochemical Impedance Spectroscopy (EIS) is being successfully applied by the conservation scientists [1] to rate the efficiency of protection offered by thermoplastic resins, clear lacquers or thin layers of wax, to the surface of heritage and art objects. Passive layers on stainless steel, rust layers on Corten steel and iron as well as patinas on copper and bronze are being probed by EIS. For such objects, application of non-liquid electrolytes was proven to be of special interest as it enables direct measurements on flat or curved surfaces and easy transfer of EIS from the laboratory into the field. Damaging of the metallic surface is the primary concern of any intervention on valuable metallic pieces, including the corrosion related measurements. Although EIS is known to be a non-destructive method, it still needs to meet high standards that tolerate no alteration of surface appearance at the place of EIS cell contact [2]. Additionally, EIS cell electrolyte should have a low enough conductivity not to interfere with the surface layer impedance that may approach that of the bare metal. The non-liquid electrolyte should also retain constant surface area during the EIS measurement, should follow the object surface pores [3] and should be easily washed of leaving no traces. In the present study, we investigate EIS characteristics of various natural wax-based paste electrolytes and their performance in measuring impedances of protective layers on metallic substrates. Flexible conductive-polymer electrodes and the electrochemical setup that has been described in our recent paper [4], were used for performing EIS measurements. Impedance spectra were measured in a broad frequency range from 10^5 to 10^{-2} Hz. Additionally, measurements on samples were repeated five times at a single frequency of 0.1 Hz, and the arithmetic mean, that varied between $k\Omega\ cm^{-2}$ and $100\ G\Omega\ cm^{-2}$, was taken as indicative of the degree of protection [5]. Surface layers of high impedance have been successfully probed by all the investigated electrolytes. Interference of electrolyte spectra with the sample spectra was seen for some electrolyte formulations on low impedance samples. The interference was visible at low frequencies and manifested itself as an increase in impedance modulus and phase angle, due to the electrolyte. Some electrolytes, although being of low conductivity, were unable to follow the pores of the substrate yielding impedance overestimate of the few orders of magnitude. The results of the good electrolyte formulations were highly correlated to the measurements obtained in the solution, in a press-on cell. The investigation exemplifies the importance of the non-liquid electrolyte consistency and electrical characteristics on the success of the surface layer impedance measurements that uses flexible conductive-polymer electrodes and is easily applicable in the laboratory and the field.

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Ion-selective sensor based on modified electrospun nanofibers – towards 2D sensing layers

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A challenge in ion-selective sensors is to reduce the ion-selective membrane thickness down to a few nanometers. Thus obtained ion-selective layers can in principle offer significant advantages both in respect to analytical parameters and applicability for current driven sensors.

We propose application of core-shell modified nanofibers mats as ultrathin ion-selective membranes for electrochemical and optical sensors[1]. Nanofibers mats are used as inert support for liquid ion-selective membrane. Thus obtained systems offer significant advantages compared to classical membranes. Due to application of nanofibers, keeping the overall macroscopic size of the recognition element as for classical plasticized poly(vinyl chloride) membranes, herein proposed systems resulted in ultrathin (< 10 nm) receptor layers with total area nearly 1000 times larger. The surface area to volume ratio of the proposed system is close to $7.5 \cdot 10^7$, making it first close to 2D potentiometric membrane. Formation of thin and continuous liquid film on nanofibers was confirmed by XPS studies. The nanofibers based ion-selective receptors used offer slope and detection limit well comparable with those for classical plasticized poly(vinyl chloride) based membranes sensors. Despite nanometric thickness of ion-selective layer, the reproducibility of recorded potentials, studied for more than 30 days, was high. Using confocal microscopy it was shown that electrolyte transport through porous nanofibers mat phase is the rate limiting step in conditioning. Estimated electrolyte diffusion coefficients for nanofibers phase are close to 10^{-10} cm^2/s, thus are orders of magnitude lower compared values characterizing ion transport through classical poly(vinyl chloride) bases membranes.

The truly nanostructural character of nanofibers based ion-selective receptors is visible in chronoamperometric experiments. It was shown that core-shell nanofibers mat behave as an array of nanoelectrodes – individual nanofibers. Thus, novel nanofibers based architecture of ion-selective receptor brings also new quality to current based electrochemistry of ion-selective sensors.

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Teaching the Electrochemistry: Between Theory and Practice

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Electrochemistry is mainly experimental science with well-established theoretical background. Today many, usually younger, researchers presents and explained experimental results that are not theoretically correct. Some of the examples are mixing concentration and activity of the species in the solution, misunderstandings of the concept of the electrode potential and usage of different reference electrodes, reporting Tafel slope as high as 0.5 to 1 V dec^{-1}, determination of exchange or corrosion current densities by extrapolating slopes of the curve under mixed activation-diffusion to reversible or corrosion potentials, etc. To avoid such confusions strong connection of the electrochemical theory and experiments.

At the Faculty of Technology and Metallurgy, University of Belgrade electrochemistry has a long history. Through generations, program of the Electrochemistry course has been changed, and today is teaching with following main subjects: Equilibrium and non-equilibrium in the electrolyte solutions, Electrodics, Electrochemical kinetics and applied electrochemistry [1]. The concept of course is based on theoretical lectures followed by experimental work for each important subjects.

In this lecture will be presented the short theoretical background and corresponding laboratory exercises, under modest experimental conditions, of the main subject of the electrochemistry, like activity and activity coefficient, Faraday law, determination of the electrode potentials and their application, thermodynamics of the electrochemical cells, kinetics of some electrode reactions under activation, mixed and diffusion control, preparative electrochemistry and specific energy consumption, corrosion and electrochemical power sources.

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"Electrodeposition + Pulling" Gel Probes for Local Electrodeposition by Scanning Gel Electrochemical Microscopy (SGECM)

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Electrochemistry is a powerful tool for locally modifying conductive surfaces by electrodeposition of etching. This is achieved through scanning electrochemical probe techniques, notably scanning electrochemical microscopy and scanning droplet cell. A recent development is to attach gel on the electrode probe and to do local electrochemistry at the interface between such gel probe and the sample (denoted as scanning gel electrochemical microscopy (SGECM)[1]). To achieve high spatial resolution, one need to sharpen the gel, which is inherently difficult due to its soft nature.

Inspired by cheese fondue, we take advantage of the thin meniscus formed while pulling a sharpened metal wire (for scanning tunneling microscopy) from a viscous chitosan precursor. At the same time, we apply cathodic potential on the metal wire to jellify chitosan based on well-known electrodeposition mechanism driven by pH modulation. This elegant "electrodeposition + pulling" approach, as illustrated in **Figure 1a**, combines electrodeposition with fluid mechanics offering sharp gel probes as shown in **Figure 1b**. The shape of the gel probes is rationally tuned by the electrodeposition and pulling parameters with good reproducibility, and the process is automated on a home-built setup as simple as pulling glass capillaries.

The sharp gel probes fabricated by "electrodeposition + pulling" are used for local electrodeposition and etching on a SGECM setup (**Figure 2a**). A model system is demonstrated, where Ag surface is oxidized to AgCl or etched by Cl^- or NO_3^- containing gel probes, respectively (**Figure 2b-c**). With the sharp gel, the lateral spatial resolution of local electrodeposition reaches *ca.* 1 µm. Moreover, due to the elasticity of the gel, one may also press or stretch the gel after contacting the sample, like writing or painting with an ink brush. That is to say, the resolution of each gel probe can be tuned in a range from a few to tens of microns. Since the gel probe immobilizes the electrolyte, it is also used for local electrochemical patterning on 3D-printed complex-shaped structures (**Figure 2d**), where the steps, steep planes and sharp edges are challenging for other techniques. Note that both the "electrodeposition + pulling" process and the local electrodeposition by SGECM are generic, with the possibility to play with the chemistry of the gel in future.

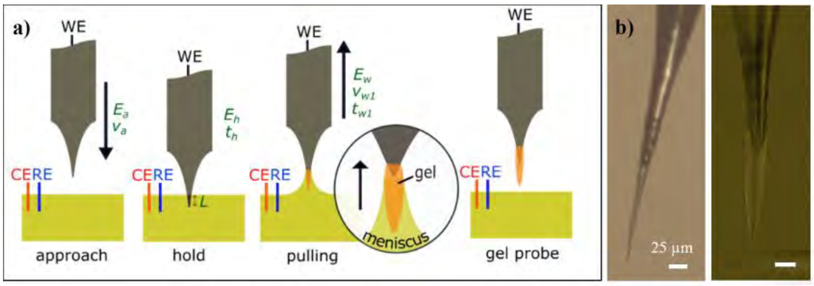

Figure 1. a) Scheme of "electrodeposition + pulling". **b)** Photos of gel probes.

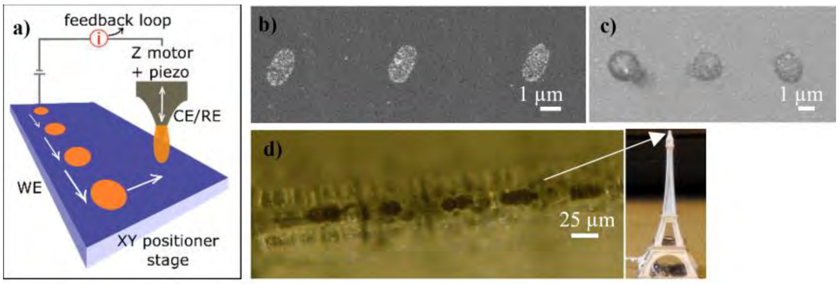

Figure 2. a) Scheme of SGECM for electrochemical patterning. **b)** Spots of AgCl on Ag plate. **c)** Etched holes on Ag-coated ITO. **d)** Dash line patterned at curved-side edge of 3D-printed Eiffel tower model.

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Diverting Electrons for Protecting Fragile Catalysts for Energy Conversion

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Widespread implementation of energy conversion devices cannot proceed without solutions that mitigate the cost of rare metal catalysts and the intrinsic O_2-instability of bio-inspired replacements. Recently, thick films of redox polymers were shown to prevent O_2 catalyst damage (1, 2), but also resulted in unnecessary catalyst load and mass transport limitations (3). Here, we apply novel methods for formation (4) and characterization (5) of homogeneous thin films that provide O_2-immunity while achieving highly efficient catalyst utilization (6). Resistance to O_2 inactivation can theoretically be obtained for non-limiting periods of time even when using highly fragile catalysts such as hydrogenases. Experimentally, the lifetimes of hydrogenases under constant aerobic turnover can reach up to one week at the condition that protection also targets reactive oxygen species (7). Different protection mechanisms operate depending on matrix dimensions and intrinsic catalyst properties, and can be integrated together synergistically to achieve large and stable H_2 oxidation currents in the presence of O_2, potentially enabling a plethora of practical applications for bio-inspired catalysts in harsh oxidative conditions.

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Insights into the ORR and OER in Ca^{2+} containing DMSO: A DEMS, RRDE, AFM and XPS study

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Calcium, being the fifth most abundant metal on earth, combines high abundance with competitive volumetric capacity. As newer studies show promising results concerning electrochemical Ca plating/stripping (1-5), a combination with an oxygen cathode promises impressive theoretical energy densities. In literature some pioneering work on the Ca $-O_2$ system exists (6-8) but deeper fundamental research is necessary to get insights into the reaction mechanism of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).

In this study we are investigating the ORR and OER in Ca^{2+} containing system with various electrochemical and analytical methods. The product distribution of ORR products is investigated with differential electrochemical mass spectrometry (DEMS) and rotating ring disc electrode (RRDE) using Pt and Au as electrocatalysts. The main products are Ca-peroxide and Ca- superoxide. Both products are soluble in DMSO. A complete blocking of the electrode surface, as it is known from Li-O_2 literature, was not observed. Still the formation of superoxide in presence of the deposited film on the electrode is observed. Characterization of the ORR products was done via ex situ XPS measurements. There we could confirm calcium peroxide and calcium superoxide as ORR products. Another oxygen containing product seems to be calcium oxide, which is located close to the electrode (shown by Ar^+ etching and XPS). In the electrochemical experiments the electrocatalysts can fully be regenerated by applying higher electrode potentials as XPS studies showed. In addition the deposition of products on the electrode was investigated with EC-AFM.

On basis of the new findings the reaction mechanism of the ORR in Ca^{2+} containing DMSO will be discussed.

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Does the most active nanocatalyst evolve the largest nanobubble?

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The (photo)electrochemical generation/conversion of gases is drawing considerable interests as a sustainable solution for energy storage or conversion. Among them, the evolution of dihydrogen gas, HER, during water splitting is one of the most actively studied processes. While numerous efforts are produced towards the design of sustainable and efficient catalysts of HER, particularly employing nanoparticles, NPs, there is a need for the *operando* observation and quantification of the gas nanobubbles (NBs) formation involved in this reaction

Single-Entity Electrochemistry offers different toolboxes to reach the ultimate goal: a benchmarking study of the intrinsic electrocatalytic activity of NP materials. However it is often limited to the study of single nanoobjects without considering the whole process such as the near neighbors effect and is technically difficult to implement. To have a wide-field overview of the NBs formation process, we coupled electrochemistry and interferometric optical microscopy. Indeed optical microscopies can image various nano-objects *operando*, and under certain conditions, both individual catalytic NPs and gas NBs can be visualized. It allowed counting at high throughput the production of NBs and therefore addressing the nucleation rate of NBs on various supports and during HER [1-3]. However, very few examples have demonstrated a quantitative and dynamic sizing of these NBs [2]. We propose such quantification process for scattering-based, label free microscopy. It allows mapping at high throughput the local gas evolution rate (NB growth or dissolution) of an electrode.

The Figure below shows example images obtained by interferometric microscopy, correlated with SEM, of the growth of individual NB at individual 40nm Pt NPs. Besides analyzing the growth rate of individual NBs, the toolbox offered by super-localization and quantitative optical microscopy allows asking relevant questions for gas evolution catalysts: do the imaged Pt NPs where H_2 is evolving have the highest electrocatalytic activity? In other words, how to correlate a gas evolution rate map to a map of NP electrocatalytic activity?

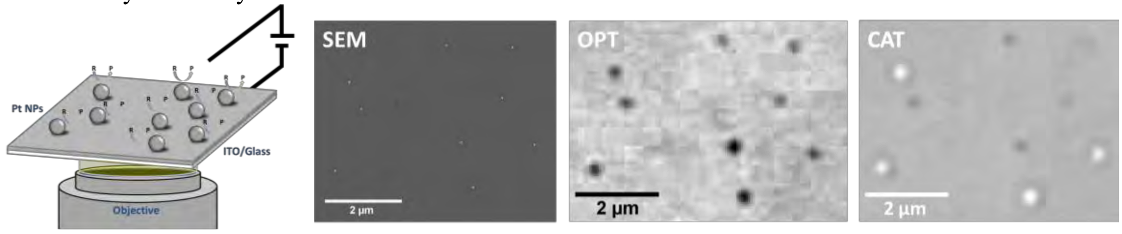

Figure: Optical monitoring of HER generation of NBs at Pt 40nm NPs. Nine single Pt NPs are imaged both by SEM and *operando* by interferometric optical microscopy before (OPT) or during (CAT) HER. The appearance of 4 bright features indicates that only 4 of the 9 NPs evolve single NBs.

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Mining Nanopore Big Data to Reveal the Single Molecule Heterogeneity

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The recent development of nanopore techniques pushes the envelope in precision and complexity to maximize the information content. Once a molecule is inside the nanopore, the signal due to the interaction of the molecule with the nanopore sensing interface is observed. Hence, the signals from individual analytes lead to an abundance of stochastic fluctuations in the shape, structure, conformation, position, and orientation of the molecule within the sensing interface.[1] These features permit single molecules to participate in unique noncovalent bonding interactions with the sensing interface of a nanopore, which in turn regulates the dynamic redistribution of ions along the sensing interface. Therefore, each ionic current response contains small ionic fluctuations, which offer continuous snapshots of the confined single molecule. After statistical time-domain analyses of duration, current amplitude, and occurrence of characteristic ionic current events as well as the frequency domain decomposition, differences in the features of single molecules, such as chemical properties, conformational changes, and charge distributions, could be detected.[2] The very beginning frequency analysis let us mine more information from the data, which could help to unravel different hierarchical pathways and enables to discovery the subpopulations and hidden kinetic during the dynamic motion of single molecules.[3-4] Together with the advanced data mining methods, we potentially show that nanopores are promising for identifying protein/peptide post-translational modification, and even decoding the sequential information.

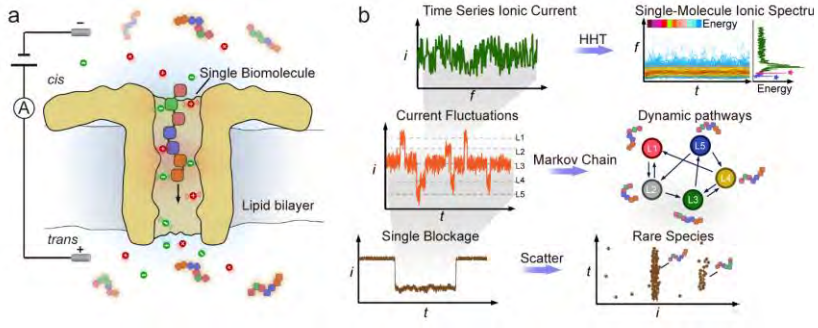

Figure 1. Nanopore-based single-biomolecule interface for single-molecule measurements. (a) A biological membrane protein molecule. (b) Information obtained from a single blockade event.

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Compositional Control of Electrodeposited Ag-Fe Films

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Composition control in electrodeposited alloys is necessary to predict microstructure evolution, phase transformations and ultimately functionality. Some alloys however are intrinsically difficult to be electrodeposited, mainly due to the large difference in equilibrium potentials and/or widely differences in reduction kinetics of the alloy components; the Ag-Fe system is one of those. In this work, a novel alkaline citrate-dimethylhydantoin (DMH) Fe(II)-Ag(I) bath has been used to synthesize Ag-Fe alloy films with several predetermined composition.

Here we demonstrate the procedure for designing a novel metastable alkaline DMH-citrate Ag-Fe electrolyte, we compare the prediction of redox potentials from thermodynamic data with the observed CV profiles, and we rationalize the composition control by exploiting limiting current concepts. Stabilization of the deposition bath was achieved by utilizing the mixed potential theory through addition of 1% of Fe^{3+} to positively shift the redox potential of the redox couple Fe^{3+}/Fe^{2+}. Alloy compositions have been predicted by imposing limiting current ratios. Little deviations from these predictions were found, probably caused by the solution metastability.

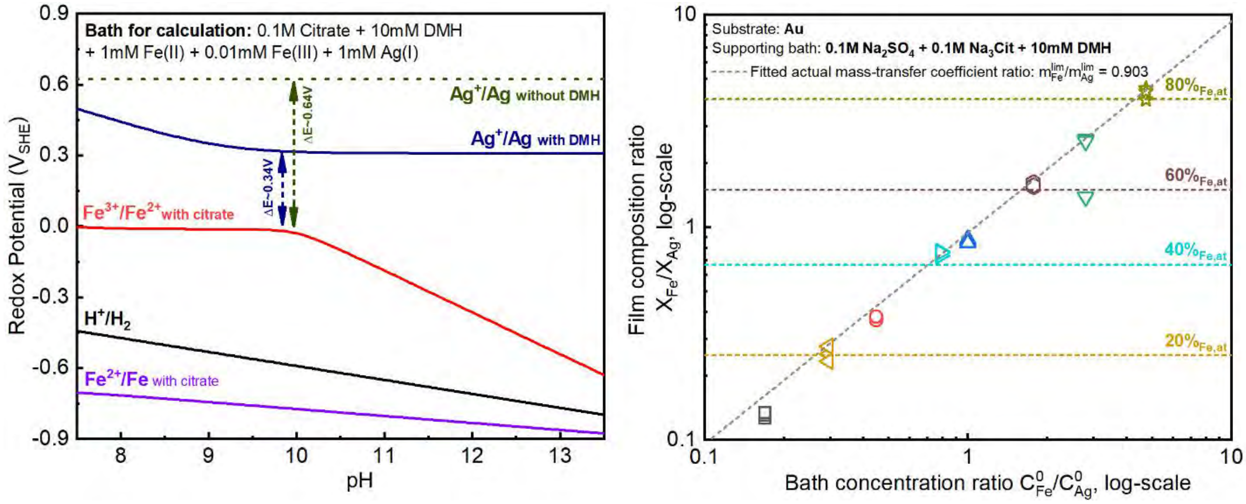

Figure 1: (a) Electrochemical equilibria calculations of the redox potentials related to the DMH-citrate complexed Ag-Fe electrolyte, based on the Nernst equation and thermodynamic data available, with the redox pair that influences the solution stability marked with arrows in the plot; (b) the stabilized bath exhibits a well-behaved linear trend between solution concentration ratio and film composition ratio.

Design of Effective Pulse Deposition Process for Functional Cr Coatings from Cr^{3+} Electrolyte

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Our work investigates the pulse current deposition process for electrodeposition of functional Cr films from Cr3+ electrolytes. Results suggest that growth stress during direct current (DC) Cr deposition is compressive with steady state values in the range below -100 MPa. The negative stress is associated with blistering in Cr films and accumulation of different defects on the surface which indicate significant amount of dissolved hydrogen either as an interstitial impurity or as a part of chemically bonded H as Cr-hydride. Our TEM data, stress, impedance and optical results undoubtedly suggest that weakened structure of the Cr films by oxidation process has a true origin in Cr-hydride formation and subsequent oxidation of its degradation by-products (H and Cr). Therefore, the electrodeposition process that produces less Cr-hydride should be more desirable when the crack and defect free Cr films are the goal.

The pulse current function design is driven by the goal to achieve Cr-films with minimum amount of Cr-hydride phase. The off time of the pulse current cycle is designed to allow break up and decomposition of hydride phase which has been formed in preceding pulse current step of the pulse cycle. The details of the pulse current cycle designed are developed upon modeling our stress relaxation transients recorded during the pulse current stage. Our in situ stress data show that using such approach, it is possible to completely change the sing of the growth stress in Cr films from compressive to tensile. More importantly, we will show the first indications that pulse electrodeposited Cr films have similar micro-cracked structure as Cr films electrodeposited from Cr6+ solutions.

This work is supported by Gift Grant from NASF-AESF Research Foundation.These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Effect of Small Amounts of Added Water in Electrochemically-Mediated ATRP in Nonaqueous Solvents

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Atom transfer radical polymerization (ATRP) is one of the most important and widely used methods of reversible deactivator radical polymerization [1]. It is mainly catalyzed by Cu complexes with N-based ligands. In electrochemically-mediated ATRP (*e*ATRP), polymerization is triggered and sustained by fast electrochemical (re)generation of Cu^I from Cu^{II} (Fig. 1a). *e*ATRP allows modulation of reaction rate through easy control of the distribution of Cu^I and Cu^{II} species in solution and the possibility of switching the process from active to dormant state and vice versa, by varying the electrochemical parameters applied to the system [2].

ATRP in water is quite challenging due to high activation rate constants (k_{act}) and equilibrium constants (K_{ATRP}). It has been reported, however, that the presence of small amounts of H_2O (~10 vol%) in organic solvents has beneficial effects on ATRP, enhancing the overall rate of polymerization without compromising control over molecular weight distribution [3,4]. The origin of this effect is not well understood although some hypothesis has been formulated mainly on intuitive basis.

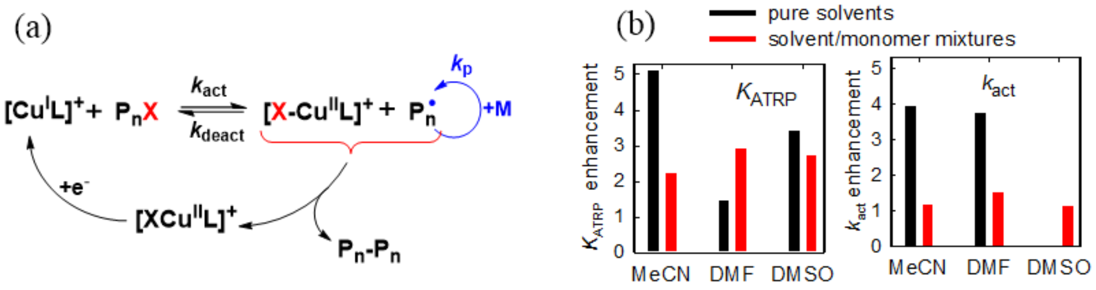

Fig. 1. (a) General mechanism of *e*ATRP and (b) effect of 10 vol% H_2O on k_{act} and K_{ATRP} in pure solvents and solvent/monomer mixtures (50/50, v/v).

We investigated the role of small amounts of water (up to 10 vol%) in *e*ATRP of methyl acrylate using $[Cu^{II}TPMA]^{2+}$ as catalyst. Experimentally, we observed an increase of the overall polymerization rate, R_p, when the reactions were performed in mixtures of MeCN, DMSO, DMF and [BMIm][OTf] with H_2O. The effect of H_2O on the redox potential of the catalyst, as well as on k_{act} and K_{ATRP} for the activation of methyl 2-bromopropionate by Cu^I was examined in pure solvents and in 50 vol% solvent/methyl acrylate mixtures. While $E^\ominus$ of the Cu^{II}/Cu^I couple was not much affected by H_2O addition, both k_{act} and K_{ATRP} were enhanced by the presence of H_2O in both pure solvents and solvent/monomer mixtures (Fig. 1b). Since R_p can be related to K_{ATRP}, the observed enhancement of K_{ATRP} may provide a plausible rationalization of the accelerating effect of H_2O in organic solvents.

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Understanding the Effects of Self-Assembled Monolayers and Nanoporous Structure on Direct Electron Transfer of Fructose Dehydrogenase

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Direct electron transfer (DET) between an electrode and redox/catalytic center(s) in oxidoreductases is a core "elementary" process in enzyme bioelectrochemistry.[1,2] Favourable orientation and high enzyme loading on electrodes are paramount in DET-type bioelectrocatalysis to ascertain high catalytic activity and ET rate.[3] Fructose dehydrogenase (FDH) from *Gluconbacter japonicas* is a membrane-bound oxidoreductase with three subunits, subunits I (67 kDa), II (51 kDa) and III (20 kDa).[4] Subunit I holds a flavin adenine dinucleotide (FAD) cofactor as the active center of two-electron fructose oxidation to 5-keto-D-fructose. Subunit II carries three heme *c* moieties, serving as ET relays between electron acceptors and FAD. Subunit III has no redox center and possibly contributes to structural integrity of enzyme.

We present here systematic investigation of the effects of both self-assembled molecular monolayers (SAMs) and nanoporous (Au-)electrode structure on DET-type bioelectrocatalysis of FDH absorbed on SAM-modified Au(111) electrodes. Two different SAMs with varying functional terminal-groups and alkyl chain lengths were studied. FDH on a 2-mercaptoethanol (BME) SAM showed the best DET performance with a maximum current density ($\Delta j_{\mathrm{max,det}}$: 54.88 ± 3.03 μA cm^{-2}) and DET-capable fraction derived from $\Delta j_{\mathrm{max,det}}$ over mediated $\Delta j_{\mathrm{max,met}}$ (χ_{det}: 13.33 %) due to the most favourable FDH orientation on the electrode surface. FDH on Au(111) functionalized with 3-mercaptopropanoic acid (MPA) SAM exhibited the best mediated ET with Δj_{max} of 640.76 ± 7.65 μA cm^{-2} using ferrocenemethanol as the mediator. This can be explained by the negatively charged SAM surface efficiently adsorbing FDH. Non-linear fitting to the electrocatalytic profiles was performed. The FDH catalytic properties strongly depend on the alkyl chain length, showing significant decrease with increasing SAM carbon chain length. Nanoporous gold supported FDH was also prepared. Porous gold structures not only improved the catalytic performance by increased enzyme loading and χ_{det}, but also increased notably the operational stability.

Acknowledgments

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Transparent cathode material for photobioelectrochemical cell development

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The combination of light-sensitive entities with electrodes has gained increasing interest in the last decade. Light can be used to switch electrochemical reactions which gives access to multiplexing by spatially resolved illumination of sensing surfaces, but it can also be used to modulate the electrochemical reactions [1]. This is interesting with respect to different aspects. One direction of research is devoted to systems which can improve the potential behavior for electrochemical signal chains. This is relevant particularly in bioenergetic applications.

Thus, we have already demonstrated the development of a photobioanode which allows the collection of electrons from the sugar oxidation at extremely low potentials under illumination. Here a combination of two semiconducting materials (TiO_2 and PbS) with a biocatalytic reaction (FAD-GDH or PSII) has been exploited [2,3].

The present study is devoted to the investigation of a material which can be prepared as a thin layer by a simple spin coating procedure on FTO slides (fluor doped tin oxide) as cathode material. The material used here is $BiFeO_3$. It is characterized by a rather high positive onset potential for cathodic photocurrents (~0.6V vs AgAgCl) and a high open circuit potential. This is based on a proper position of valence and conduction band of the material. When hydrogen peroxides is added to the solution the cathodic signals can be significantly enhanced - although there is no electrochemical H_2O_2 reduction in the dark at the electrode. The generated photocurrent provides sufficient stability with millimolar hydrogen peroxide concentrations and a defined dependence on the light intensity and H_2O_2 concentration.

This provides the basis for the construction of a photobiocathode with a rather high potential by coupling an enzymatic reaction to the photoactive electrode.

These investigations may illustrate the potential of coupling suitable semiconductor structures with biocatalytic conversions on electrode surfaces for application in bioenergetics but also in biosensing.

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Spectroscopic study of the Na$^+$ insertion mechanism and SEI formation in bio-waste derived hard carbon anodes for sodium-ion batteries

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In the continuously growing field of post lithium-ion batteries (LIBs), sodium-ion batteries (SIBs) have emerged as a prominent candidate and valid alternative solution to the Li-ion technology, especially in systems dedicated to large-scale stationary energy storage. The abundance and availability of sodium reserves, combined with the low use of critical raw materials have sparked the investigation of high performance and efficient electrode materials for SIBs.

Currently, hard carbon (HC) represents the anode of choice for SIBs. Bio-waste derived HC, in particular, is very attractive in terms of sustainability, cost and electrochemical properties [1,2]. However, the processes governing the electrochemical performance of HC anodes are not completely understood, most likely stemming from the lack of a widely agreed-upon model of the HC structure, which hinders a comprehensive description of the processes occurring upon sodiation and its effects on the electronic and structural configuration of the materials. For example, the formation of the solid electrolyte interphase (SEI) layer and the sodium ions' uptake and release are two crucial processes affecting the battery lifetime and performance. Several mechanisms have been proposed so far, however, a universally accepted mechanism governing these reactions is still largely discussed [3,4].

This study aims at using powerful chemically sensitive synchrotron-based fluorescence and photoelectron spectroscopies to elucidate the composition and structure of complex materials. In order to gain insights into the SEI formation and the Na uptake in the underlying HC anode, a combined approach of X-ray spectroscopies with a tunable probing depth is used allowing differentiation of the spectral contributions of the bulk electrode from those related to the SEI layer. HC-based electrode samples have been investigated at different stages of (dis)charge using X-ray absorption (XAS), emission (XES), and photoelectron spectroscopy (XPS) in the soft and tender X-ray regimes, revealing the formation and evolution of the SEI during the initial sodiation process and subsequent cycles. The chemical species observed in the SEI mainly originate from the decomposition of the salt and the carbonate-based electrolyte, as also shown with *post mortem* Fourier-transform infrared spectroscopy (FT-IR) measurements. Additionally, resonant inelastic X-ray scattering (RIXS) measurements at the C K-edge provide supplementary information about the Na-insertion mechanism into the anode structure due to its excellent atom-specificity and mapping of the C band structure at different (dis)charge stages. The study has been complemented with an in-depth investigation of the structural changes of the HC electrode upon (de)sodiation by *in situ* Raman spectroscopy. This comprehensive spectroscopic study provides new insights into the complex mechanisms governing the sodium insertion and the SEI formation in hard carbon anodes.

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Micro-scale capacitive-faradaic fuel cells for ions separation from water

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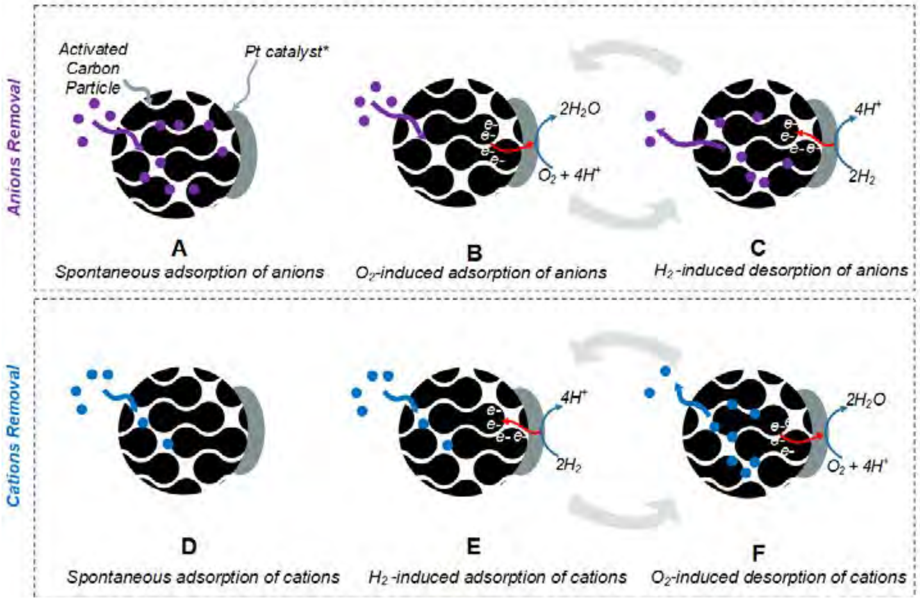
A novel method for separation of ions from water and wastewater using micro-scale (10µm – 5 mm) fuel cells has been recently proposed[1]. The fuel cells comprise activated carbon particles loaded with bifunctional catalyst for hydrogen oxidation and oxygen reduction reactions. Within the proposed process of ions removal, the particles act as *micro-scale capacitive-faradaic adsorbing fuel cells* (*MS-CF-AFC)* which require oxygen and hydrogen gases for adsorption of ions during the water treatment step and desorption of ions in brine production. The process was proved for removal of perchlorate ions from $NaClO_4$ solutions in deionized water and groundwater using batch and packed-bed reactors for two types of *MS-CF-AFCs* prepared from Lewatit AF5 microporous carbon and a powdered activated charcoal loaded with Pt (5wt%) catalyst. Within the O_2-induced adsorption of ClO_4^- ions, the reduction of oxygen on Pt (faradaic electrode of the *MS-CF-AFC*) results in depletion of electrons from the carbonaceous part (i.e. the capacitive electrode) of the micro-scale fuel cell, which leads to adsorption of anions in the electrical double layer. The hydrogen oxidation that occurs during the regeneration of the ClO_4^-- loaded *MS-CF-AFCs* results in accumulation of electrons in the capacitive electrode and in repulsion of perchlorate ions into the regenerant solution. This way the chemical energy of H_2 and O_2 is converted by the *MS-CF*-AFCs into the electrical energy which is utilized for separation of ions. The technique was proved for separation of cations as well in batch mode experiments of Cu^{2+} ions separation from $CuCl_2$ solutions. In this case the *MS-CF-AFCs* were powered by H_2 gas during the Cu^{2+} adsorption step and by O_2 gas in brine production.



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Accelerated discovery of next-generation battery materials and interfaces

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Secondary batteries play a crucial role in the transition to a clean energy infrastructure, but until now, the development of novel, low-cost, high capacity and/or high voltage electrode materials, has been too slow. Understanding and controlling the complex and dynamic processes taking place in the electrodes, electrolytes and in particular at the battery interfaces/interphases holds the key to develop more durable ultra-high performance batteries. Atomic-scale simulations have reached predictive accuracy in many critical areas of materials design and characterization, e.g., the identification of rate- and potential limiting reaction steps. Here, we provide recent examples of how density functional theory (DFT) simulations supported by AI, machine learning and cluster expansion techniques [1] can been used to identify the limiting thermodynamic, ionic and electronic charge transfer mechanisms in next-generation electrode materials and interfaces [2-3], and how interfacial dopants and additives can be used to improve their performance [4]. Finally, we will discuss the "Battery Interface Genome – Materials Acceleration Platform" (BIG-MAP) project in the large-scale European research initiative Battery 2030+, focusing on simultaneous utilization of data from multiple domains. BIG-MAP aims to accelerate the materials and interface discovery process for batteries, and here, we present our perspective on AI-orchestrated discovery of batteries using autonomous workflows [5] and generative deep learning models to control and ultimately (inverse) design better battery interfaces [6]. These models are trained on all sources of available data, i.e., large-scale multi-fidelity data sets, multi-scale computer simulations and databases, operando X-ray and neutron characterization from large-scale research facilities, high-throughput synthesis and laboratory testing.

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$H_2V_3O_8$ as model system for ion insertion

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Since the elucidation of the Lithium-Ion shuttle mechanism many developments and investigations in the battery field were enabled.[1-4] The mechanism consists of the idea of shuttling a specific ion (*e.g.* lithium ion) between two host materials with a sufficient electrochemical potential difference in order to electrochemically store energy.[5] This basic principle of energy storage was transferred to other cations, *e.g.* Na^+, K^+, Mg^{2+}, Ca^{2+}, Zn^{2+} or Al^{3+} aiming for novel/other metal-ion battery (MiB) systems.[3, 4, 6, 7] While very promising candidates for each MiB system are under investigation, only few materials have been discovered which can intercalate more than one specific ion with substantial capacities. This is due to the different chemical properties and the electrochemical behavior of the investigated ions. However, this is a very general statement and only little attention has been paid to the reasons why materials work exclusively for one specific insertion cation.

A promising material to address the question, which parameters dominate the electrochemical storage behavior is $H_2V_3O_8$ (HVO), since Li^+, Na^+, K^+, Mg^{2+} or Zn^{2+} can be inserted.[8-11] While each work proved exclusively that HVO is as promising host material for the investigated insertion ion, neither conclusions nor comparisons were made with respect to the different ion storage behaviors, such as which crystallographic position will be occupied or why and how the crystallographic structure changes during the insertion process. Answering these questions, however, has the potential to provide insight into the storage behavior. From there conclusions can be drawn why this material is so versatile in the uptake of various insertion ions and which parameters lead to this behavior.

In this contribution, we present new insight in the $H_2V_3O_8$ structure and why this material is a promising candidate to investigate the needs which must be addressed as a function of the insertion ion. In particular, we will discuss the influence of structural modifications and, for the first time for this material, of the operating temperature on the storage behavior of various cations (*i.e.* Li^+, Zn^{2+}). The obtained electrochemical and structural results will be discussed and compared with respect to the different insertion ions.

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Nanoscale visualization of cell surface under Epithelial-Mesenchymal Transition by Scanning Ion Conductance Microscopy

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Background of this research

Epithelial-mesenchymal transition (EMT) is a process that epithelial cells lose epithelial features and acquire mesenchymal characteristics. This phenomenon progresses for a few days with changing adhesion structures at nanoscale until losing cell-cell adhesion. As a result, EMT brings about cancer invasion and transition with morphological variations, and it is also known that there are only two states (Epithelial state to Mesenchymal state) under EMT. Recently, some researchers reported that there was some intermediate states with differences of gene expression between two states[1]. However, continuous dynamics of cell surface is not comprehensively understood at nanoscale by conventional analytical techniques. Therefore, tracking nanoscale morphological changes are necessary throughout a few days to investigate the intermediate states. In this study, we visualized topographical changes on cell membranes at nanoscale by scanning probe technique.

Scanning Ion Conductance Microscope

Scanning ion conductance microscopy (SICM) is one of scanning probe microscopies for visualizing nanoscale topography of cell surface without invasion[2]. Figure 1 shows a schematic illustration of SICM. A glass nanopipette (tip diameter: 100 nm) filled with medium and Ag/AgCl wire is used as a probe. When a voltage is applied between the nanopipette and the medium, ionic current due to ionic flow through the probe is measured. The ionic current is used as a feedback signal to control the distance between the probe and a sample surface[2]. Nanoscale images can therefore visualize without physical contact and fluorescence labelling.

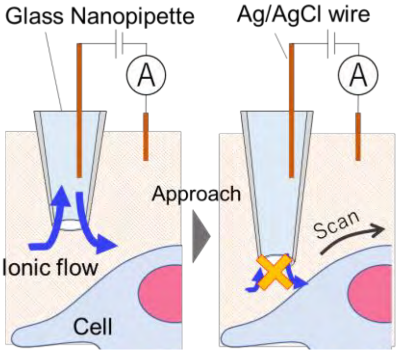

Figure 1: Schematic illustration of SICM

Experiments, results and future works

A549 cells (Human alveolar adenocarcinoma cell line) were used as a model of epithelial cells. Before EMT process, multiple microvilli were observed on A549 cell surface by SICM. After treatment with 10 ng/mL TGF-β in the culture medium, microvilli decreased within 6 days. From immunostaining results, A549 lost E-cadherin within 5 days. The process of losing cell-cell adhesion can be observed by SICM. These results indicated that the EMT was progressed by treatment of TGF-β, and the membrane remodeling was visualized at EMT transition states by SICM. Currently, we have developed a combined SICM system with an incubator that can achieve long-term measurement to understand intermediate states in EMT. We expect that this technique will be useful for understanding the mechanism of EMT.

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Photosystem I Monolayers with Controlled Orientation for the Fabrication of Energy Conversion Devices

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Photosystem I (PSI) is one of the key protein complexes driving oxygenic photosynthesis, a highly developed process by Nature through billions of years of evolution for the efficient conversion of sunlight into chemical energy. Resembling a photodiode, PSI is able to perform charge-separation upon absorption of visible light, with a considerably high quantum efficiency for the photon-to-electron conversion process. After subsequent internal electron transfer, a final state is obtained at PSI, consisting of two redox centers of opposite charge with a potential difference of about 1.0 V. In addition, PSI is a robust and widely abundant biomolecule. As a result, PSI is considered an attractive building block for the fabrication of semi-artificial energy conversion devices. However, a consequence of the large voltage difference between the terminal redox sites at PSI is that it translates directly into a substantial driving force for recombination and short-circuiting processes, as a result canceling out at least part of the generated photocurrents in conventionally implemented devices [1,2]. Therefore, one of the major challenges in the development of PSI-based photobioelectrodes constitutes the fabrication of well-defined structures able to provide a unidirectional electron flow.

Taking advantage of the amphiphilic nature of PSI, the molecule can be used for the preparation of dense Langmuir monolayers. After spreading isolated PSI protein complexes onto a water-air interface, the hydrophilic ends adopt a specific orientation either being solubilized in water or facing air, while the hydrophobic regions stack together after compression of the movable barriers at a Langmuir trough. Since the terminal redox centers at PSI are located at opposite sides of the biomolecule within the hydrophilic ends, a densely packed and stable monolayer presenting a preferential orientation is obtained. This molecular structure can be transferred to the electrode surface for the fabrication of PSI-based biophotoelectrodes presenting an anisotropic electron flow [3]. On this basis, novel architectures for the fabrication of PSI-based photobioelectrodes are presented, enabling the development of more efficient solar-to-chemical energy conversion devices as a result of the decreased charge recombination and short circuiting processes.

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How Theory Can Help Us with Engineering Graphene-Based Materials for Electrochemical Applications?

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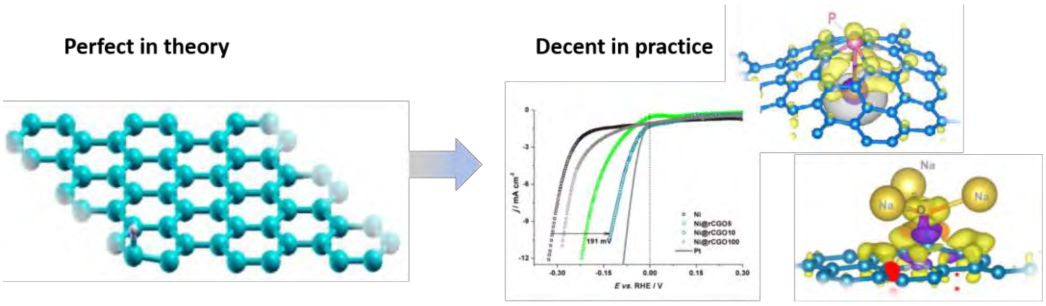
Since its discovery, graphene attracts immense attention of the scientific community and it is frequently claimed to be the perfect material for numerous applications. It is not surprising that graphene quickly found its place in electrochemical laboratories. This is natural because electrochemists have been using carbon materials for decades, and graphene indeed possesses some properties which are attractive to electrochemists. High conductivity and large specific surface are some of them. However, perfect (pristine) graphene is chemically inert and reacts poorly with basically any atom in the Periodic Table of Elements [1]. Luckily, it turns out that for electrochemists pristine graphene is not so interesting. Much more can be obtained by the introduction of defects and functional groups on graphene basal plane and edge sites, pawing a way to new battery materials, materials for electrochemical capacitors or electrocatalysts. However, to fully exploit the potential of graphene-based materials an atomic level of understanding is a must, and theoretical methods can help us along this path. We shall present some of the recent results of our group on the modelling of graphene-based materials for energy conversion applications. First, we shall address some general features of functionalized graphene surfaces with heteroatoms and oxygen functional groups [2] and demonstrate such functionalization can be employed in metal-ion batteries [3]. Then we shall address the tailoring of graphene-oxide for the applications in electrochemical capacitors [4]. Finally, we shall describe how different levels of theory can be used to guide the development of novel graphene-based platinum-free electrocatalysts for hydrogen evolution [5]. We intend to present a realistic situation in the field, demonstrating possibilities, but also limitations of the use of graphene-based materials in electrochemistry.



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Spectroelectrochemical study of water oxidation on nickel-based electrocatalysts in alkaline solution

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Efficient (photo)electrochemical oxidation of water is pivotal to the production of energy carriers such as hydrogen, ammonia, synthetic carbon-neutral fuels by CO_2 reduction and the production of metals from metal oxides[1]. Nickel-based oxides have been widely employed as water oxidation catalysts in alkaline electrolyte owing to their high intrinsic activity and stability[2,3]. In order to understand and further improve the activity of catalytically active centers, it is imperative to understand the reaction mechanism and atomic scale processes occurring during water oxidation. Specifically, nickel-based oxides form an oxyhydroxide structure under oxidizing conditions relevant to water oxidation[4], which have layered structures, with varying degrees of long-range order. Water and electrolyte ions can intercalate within the resultant three-dimensional structure to access redox states within the bulk, beyond the surface and sub-surface layers[5]. Thus, both, the intrinsic activity for water oxidation and the density of accessible active sites need to be increased in order to design the most active catalysts.

In this study, we use *operando* spectroelectrochemical methods[6] to assay the concentration of oxidized species for a series of metal-doped NiO films ($M_{0.1}Ni_{0.9}O$, M = Fe^{3+}, Co^{2+}, Mn^{2+} and Zn^{2+}) synthesized from the respective chloride salts. We first demonstrate how the dopant atoms can be used to rationally tune the binding energetics of the Ni site for water oxidation. The density of oxidized species accumulated under reaction conditions at potentials between 1.5 V_{RHE} and 1.8 V_{RHE} decreases in the order $Mn_{0.1}Ni_{0.9}O > Co_{0.1}Ni_{0.9}O > Fe_{0.1}Ni_{0.9}O > NiO > Zn_{0.1}Ni_{0.9}O$, which correlates with the onset of the Ni^{2+}/Ni^{3+} redox peak position, i.e. the accumulation of redox species is greatest for chemistries that are easiest to oxidize. On the other hand, we find that the kinetics of water oxidation, defined as the turn over frequency per active oxidized species, increases from $Mn_{0.1}Ni_{0.9}O$ to $Co_{0.1}Ni_{0.9}O$ and $Fe_{0.1}Ni_{0.9}O$ but decrease for NiO and $Zn_{0.1}Ni_{0.9}O$, demonstrating a volcano relation where the ideal Ni site binds oxygen neither too weakly nor too strongly. In the next part of this study, we use different precursor salts (chloride, nitrate, sulfate, triflate) to synthesize the metal oxides, which results in a change in the local structural environment around the active site. Differences in local structure are manifested as changes in the rates of generation of oxidized species as a function of potential, suggesting that the accessibility of active sites is influenced strongly by the local structure around the active site. Thus, based on the use of combined optical and electrochemical techniques, we highlight possible strategies to enhance the activity of Ni-based oxides by tuning both the intrinsic activity per active site by modifying the electronic structure as well as the accessibility and utilization of these sites.

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Detection of cancer-related glycosylation changes in prostate specific antigen using electrochemical label-free aptasensors

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Cancer is associated with aberrant glycosylation and each type of malignant issue is characterized by a distinct change in the glycan structure. Therefore, analysis of tumor-linked glycan alterations is proposed as a valuable tool for diagnostic and prognostic purposes. The glycosylation profile of tumors is currently characterized by long and complicated protocols, based on final MS detection or with the use of lectins. However, these procedures cannot be applied for routine analysis in early detection of cancer. In consequence, to translate these biomarkers from discovery to clinical diagnostics there is a clear need for extremely selective methods, able to differentiate the glycan profile characteristic of disease conditions. Aptamers can be tailored to specifically detect aberrant glycosylation at each protein or even at each glycosylation site, and the use of aptamers as synthetic receptors appears to be a promising approach to replace the current methods [1]. In the case of the prostate cancer, it has been recently described that there is a variation in the fucose and the sialic acid in the glycan structure of the Prostate Specific Antigen (PSA), the only biomarker approved for clinical use in this type of cancer. This aberrant glycosylation is a better marker of the aggressiveness of prostate cancer. [2]

In this work we present a strategy to direct the selection of aptamers toward the glycosylation site of the protein PSA, both glycan and surrounding peptide moieties. The SELEX procedure is based on counter-selection steps against the recombinant PSA (unglycosylated) and two different strategies using lectins. The aptamers in the last cycle are cloned, sequenced and classified into families using bioinformatics tools. The most abundant aptamers are characterized by electrochemical binding assays. The best aptamer is able to recognize specifically the glycans of the protein PSA due to the interaction with aminoacids of the protein but does not recognize other glycoproteins.

We employed the as-selected aptamer or an aptamer previously described for PSA, which only recognizes the peptidic part [3], for the development of an impedimetric label-free aptamer-based sensor, onto home-made gold electrodes modified with gold nanoparticles as support of the sensing phase. With both aptamers we obtained two different calibration curves for the analysis of the total PSA and glycosylated PSA. The sensor responds to different levels of total PSA in human serum reaching levels well-below the 4 ng/mL cut-off. These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

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Material Screening Revisited: Challenging the Paradigm of a Thermoneutral Electrocatalyst as Apex of a Volcano Plot

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On the way toward a sustainable energy scenario, environmentally friendly and efficient electrocatalysts need to be developed. Material screening is a promising strategy to recognize potential electrode and electrolyte compositions. Most researchers apply the volcano approach, as introduced by Nørskov, Rossmeisl, and co-workers, which connects Sabatier's principle and the Brønsted-Evans-Polanyi relation to the analysis of simple binding energies, while neglecting the applied overpotential and kinetics in the analysis **[1]**. This methodology purports that an optimum electrocatalyst stabilizes all reaction intermediates thermoneutral at zero overpotential ($\Delta G_{\mathrm{RI}} = 0$ eV at $\eta = 0$ V).

Recently, the author derived material-screening approaches that pay proper attention to the applied overpotential and kinetics: while the concept of kinetic scaling relations enables resolving the rate-determining reaction step within a homologous series of materials at overpotentials corresponding to typical reaction conditions **[2,3]**, overpotential-dependent volcano curves enclose the applied overpotential into the determination of the volcano's apex **[4-6]**. These advanced methods have been connected to Nørskov's theory by establishing a unifying material-screening approach **[7,8]**, which has shown to excel the conventional volcano scheme with respect to thorough sorting of electrode materials into active and inactive catalysts **[9]**.

Most notably, the inclusion of the applied overpotential and kinetics into the volcano concept indicates that optimum electrocatalysis requires thermoneutral bonding of the crucial reaction intermediate at target overpotential ($\Delta G_{\mathrm{RI}} = 0$ eV at $\eta > 0$ V), that is, endergonic bonding at $\eta = 0$ V. This result was corroborated by microkinetic modeling **[10]**, giving rise to reappraise the traditional understanding of the volcano approach for electrocatalytic processes: electrocatalysts that bind the decisive reaction intermediate endergonically at $\eta = 0$ V are not necessarily catalytically inactive, whereas the opposite case holds true, that is, exergonic bonding of reaction intermediates at $\eta = 0$ V results in a poor catalytic activity. Consequently, electrocatalysts with $\Delta G_{\mathrm{RI}} > 0$ eV at $\eta = 0$ V should not be discarded when conducting volcano analyses (cf. **Figure 1**).

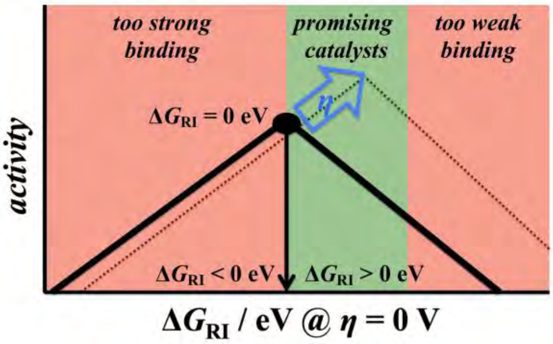

Figure 1: The apex of the volcano curve for a simple two-electron process shifts toward weak bonding when the applied overpotential and kinetics are included in the analysis.

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The Influence of Protic and Aprotic Ionic Liquids on the Electrochemical Behavior of Organic Radical Polymers

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Organic radical polymers (ORPs) have received a growing interest over the last decades, as they combine fast kinetics with typical characteristics of organic redox active materials like flexibility, sustainability and versatility [1]. Today one of the most investigated ORPs is poly(2,2,6,6-tetramethylpiperidinyl-N-oxymethacrylate) (PTMA), which was first introduced by Nakahara et al. in 2002 [2]. PTMA bears a 2,2,6,6-tetramethylpiperidinyloxy-group (TEMPO) in the repeating unit and thus provides a theoretic capacity of 111 mAh g^{-1} and a high rate capability as well as high cycling stability [3]. Most of the work dedicated to PTMA-based electrodes has been done utilizing typical lithium-ion batteries (LIBs) electrolytes e.g. 1M lithium hexafluorophosphate in ethylene carbonate/ dimethyl carbonate (1M $LiPF_6$ in EC/DMC). Little effort has been directed towards the use of ionic liquids (ILs), although these electrolytes - which could be used neat, in mixtures with organic solvents or in gel polymer electrolytes - could be interesting for the development of advanced polymer-based energy storage devices. [4],[5]. In one of our previous studies, we were able to show that the use of neat 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($Pyr_{14}TFSI$) has a positive effect on the cycling stability as well as the self-discharge behavior of PTMA in a metal-free setup [6].

In this work, we performed a systematic analysis of the electrochemical behavior of PTMA-based electrodes in combination with two aprotic and two protic ILs. Namely $Pyr_{14}TFSI$, 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide ($Pyr_{14}FSI$) (aprotic), 1-butyl-pyrrolidinium bis(trifluoromethane-sulfonyl)imide ($Pyr_{H4}TFSI$) (protic) and 1-butyl-pyrrolidinium bis(fluorosulfonyl)imide ($Pyr_{H4}FSI$) (protic). By doing so, we were able to show that the nature of the cation and the anion of the ILs has a strong impact on the performance of PTMA. Furthermore, we demonstrate that when neat $Pyr_{14}FSI$ is used as electrolyte, PTMA-based electrodes display outstanding stability for 2.5 months during float experiments carried out at a potential of 1.1 V *vs. Ag* (corresponding to 4.1 V vs. Li/Li^+) (Figure 1).

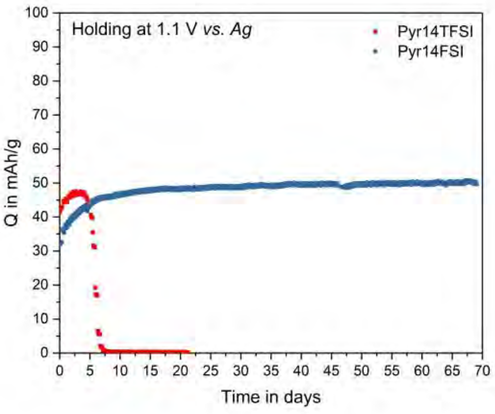

Figure 1: Capacity retention of PTMA based electrodes in $Pyr_{14}TFSI$ $Pyr_{14}FSI$ after 70 days of floating at 1.1V vs. Ag (corresponding to 4.1 V vs. Li/Li^+)

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Nanostructured Pt_xM/C (M = Cu, Co, Ni, Ir, Y) Alloy Electrocatalysts Synthesized via a Novel Top-Down Route Towards the Enhancement of the ORR Activity

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Addressing the sluggish kinetics of the oxygen reduction reaction (ORR) which occurs on the cathodic end of the fuel cell is of peculiar interest for future sustainable energy conversion and storage in the automotive industry to be specific. Continuous search for an optimum catalyst to address this challenge has led to the discovery of Pt-based nanostructured alloys as prominent candidates. As such, alloying nanostructured Pt with 3d transition metals and/or rare-earth elements is an auspicious approach to tune the electrocatalytic activity towards the ORR. Usually, bulk Pt-alloys are used in the synthesis of nanostructured Pt-alloys. With the exception of Pt_xIr nanoparticles (NPs) that were synthesized from their bulk metal alloys, all the other NPs investigated in this study were synthesized using a different strategy or method. For the first time herein, this study presents the direct dissolution and/or deposition of 3d transition metal/rare-earth element precursor salts into the 1.0 M KOH electrolyte to produce NPs from bulk Pt. By so doing, nanostructured Pt_xM/C (M = Cu, Co, Ni, Y) alloys were synthesized using a novel top-down nanostructuring technique which is the electrochemical erosion of bulk metal and/or metal alloys. The nanoparticles were characterized using transmission electron microscopy, energy-dispersive x-ray spectroscopy, x-ray diffraction and spectroscopy. The electrocatalytic oxygen reduction activity for the various nanocatalysts were also measured.

All the synthesized samples apart from the leached Pt_xY/C-15V exhibited specific activities (SAs) higher than the reference Pt/C TKK catalyst. In terms of mass activities (MAs), aside Pt_xNi/C-10V and Pt_xY/C-15V that displayed lower MA compared to the reference Pt/C TKK catalyst, all the other investigated nanostructured electrocatalysts outperformed the reference Pt/C TKK catalyst. In particular, Pt_xCu/C-15V showed a 4 fold enhancement (0.64 A/mg_{Pt} at 0.9V vs RHE) in terms of mass activity and ~ 5.5 fold higher specific activity (2.27 mA/cm^2 at 0.9V vs RHE) when compared to the reference Pt/C TKK catalyst.

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In-situ electrolytes for high performance electrical double layer capacitors

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Electrical double layer capacitors (EDLCs) display high power, high cycle life and high safety and, due these favorable features, they are nowadays considered one of the most interesting energy storage systems [1-2]. The properties displayed by EDLCs are originated by the storage mechanism taking place in these devices, which is relying on the formation of an electrical double layer at the interface between electrodes and electrolyte. The state-of-the-art EDLCs consist of composite electrodes containing highly porous activated carbons (AC) as active materials and electrolytes based on a salt dissolved, in most of the cases, in an organic solvent.

Nowadays, the AC utilized in EDLCs are typically realized through the chemical activation of carbonaceous precursors. This process is allowing the realization of designed AC, able to display high capacitance. However, the overall process is resource consuming and it requires several washing steps to separate carbon and activation reagents [3]. For this reason, its optimization would significantly improve the overall sustainability of EDLCs.

In this work we present a holistic concept, indicated as "in-situ electrolyte" in which by-product salts, which are formed during the synthesis of AC are not considered as waste products but rather upcycled to an organic electrolyte for EDLC application [3-4]. Thereby, the waste production during the EDLC preparation is minimized greatly (with an increase of the mass productivity of 15-fold) and only the use of a solvent is required for the realization of EDLCs. We showed that EDLCs realized utilizing the "in-situ electrolyte" approach display high capacitance at high current density (30 F g^{-1} at 10 A g^{-1}) and high cycling stability.

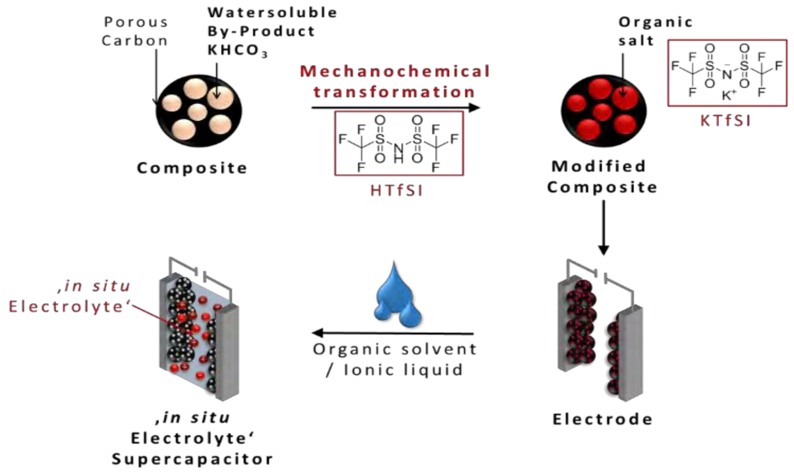

Figure 1. Schematic representation of the in-situ electrolyte approach

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Quick Determination of Electroactive Surface Area of Some Oxide Electrocatalysts

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Metal oxides are important functional materials with a wide range of applications, especially in the field of electrocatalysis. However, quick and accurate assessment of their real electroactive surface area (ECSA), which is of paramount importance for the evaluation of their specific activity, remains a challenging task. In the presentation, I will present a relatively simple strategy for an accurate *in situ* determination of the ECSA of commonly used metal oxide catalysts, namely: Ni-, Co-, Fe-, Pt- and Ir-based oxides. Similar to the well-established practice in electrocatalysis, the method is based on the phenomenon of specific adsorption. It uses the fact that, at the electrode potentials close to the onset of the oxygen evolution reaction (OER), specifically adsorbed reaction intermediates manifest themselves through so-called adsorption capacitance, which is unambiguously detectable using electrochemical impedance spectroscopy.[1,2] With simple impedance measurements, experimentalists can acquire the adsorption capacitance values and accurately estimate the real electroactive surface area of the above-mentioned oxide materials, including nanostructured electrocatalysts. Additionally, as illustrative examples, I will demonstrate an application of the method for the determination of the ECSA of oxide catalyst nanoparticles.

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Vesicular Neurotransmitter Release is Altered by Zinc Cations as Evidenced by Amperometry and Kinetic Modelling

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Zinc is an important nutrient playing important role in metabolic processes (cell growth, DNA transcription etc.). At the same time, there is a mounting evidence of zinc being involved in potentiating learning and memory, although the mechanism of zinc action on the latter processes is not clearly identified and understood.

In this work, the effects of Zn^{2+} cations on the exocytosis in PC12 cells was studied. Zn^{2+} cations were shown to influence exocytotic release and storage in neurotransmitter-containing vesicles. In order to characterize and quantify different aspect of this complex process a combination of several techniques was used. Transmission electron microscopy (TEM) was employed for structural analysis and size measurements of the vesicular dense core and halo (less compacted zone), while single-cell amperometry allowed investigating the vesicle fusion pore size changes induced after zinc treatment. The amperometric traces before and after Zn^{2+} treatment were analyzed and compared to theoretical predictions based on the concept of partial release as opposed to full quantal release and incorporating structural information obtained from TEM.

This powerful combined analytical approach allowed establishing the existence of an unsuspected strong link between vesicle structure and exocytotic dynamics. These results allowed delineating possible mechanism of regulation of synaptic plasticity by Zn^{2+} through modulation of kinetics and amount of neurotransmitter release [1].

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Electrochemical impedance spectroscopy with nanoporous structures composed of nonconductive polystyrene nanoparticles

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Electrochemical impedance spectroscopy (EIS) is a suitable method for in-depth studies of interfacial processes. As its output signal is a function of applied potential modulated in frequency domain (instead of time), lots of information can be gathered from a single measurement. Using EIS, we investigated solid-state nanoporous interfaces formed by assembling nonconductive polystyrene nanoparticles in densely packed layers on the electrode (Figure A). Due to the dense hexagonal packing, the interstitial space among three neighboring nanoparticles can be considered as a nanopore of specific diameter. Monolayers composed of carboxylated polystyrene nanoparticles different in size were tested. These monolayers were further modified with protein (human serum albumin) with the intention to reduce the dimensions of the nanopores and to monitor the corresponding electrochemical impedance behavior. Moreover, ordered multilayer structures of nanoparticles, built layer-by-layer, were investigated throughout the same experiments. Unexpected and interesting outcomes were acquired. The absolute impedance of the monolayers corresponded to the level of carboxylation of the particular nanoparticles apart from the influence of reduced nanopores (Figure B, C; Sopoušek et al., ACS Appl. Mater. Interfaces, 2020, in press). The impedance spectra of multi-layered structures exhibited additional resistance component (Figure D). All impedimetric data were fitted with theoretical equivalent circuits and the interfacial effects in such matrices were discussed.

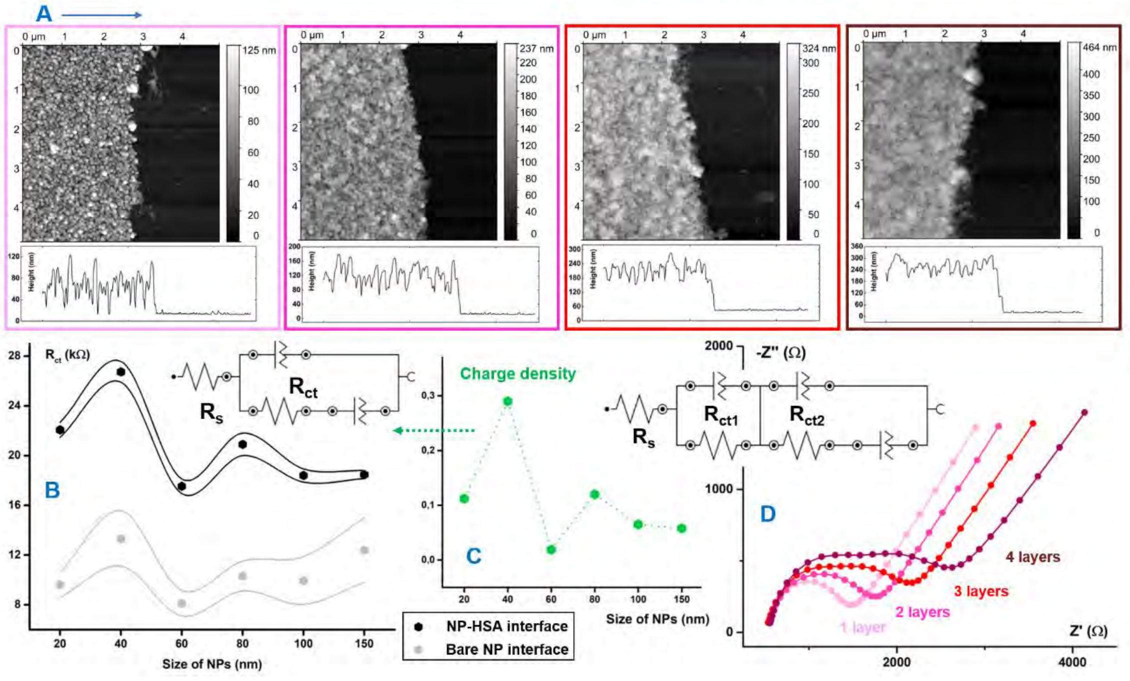

Figure: A: Visualization of the nanoporous structures composed of 80 nm nanoparticles using AFM (including heights in cross-section). B: Charge transfer resistance (R_{ct}) of un/modified monolayers of nanoparticles containing nanopores of different diameter. The strange behavior corresponds to the level of carboxylation of individual nanoparticles in C. D: Impedance spectra of multilayers indicate additional resistance component.

Acknowledgements

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The importance of double layer charging and electrolyte composition in electrochemical CO_2 reduction

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Electrochemical CO_2 reduction is a particularly challenging process from both modelling and experimental perspectives. The challenge arises from the complexity of its reaction network and the sensitivity of its activity and selectivity to the electrolyte composition and the associated interfacial field effects. In this talk, I will first discuss developments in methods to model the electrochemical interface - the accuracy of widely applied continuum approximations of the electrolyte, as well as a new unified approach to obtain electrochemical barriers from both explicit and implicit solvent simulation approaches. In particular I emphasize that the surface charge gives the most appropriate proxy of the local potential (vs. the traditionally considered work function). Then, I will discuss the impact of the electrolyte composition - pH and ions - on electrochemical CO_2R activity of both transition metals as well as supported single atom catalysts. Finally, I discuss the implications of our findings for electrocatalyst design and electrolyte engineering.

Reaction Confinement Enables High-Capacity and Stable Anodes for Alkali-Ion Batteries

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Current insertion anode chemistries are approaching their capacity limits; thus, battery technologies have to move toward the employment of electrode materials based on “multi-electron redox reactions”. Materials based on alloying reactions offer this characteristic, enabling the storage of a few alkali ions and electrons per host atom. In particular, silicon and germanium are considered as potential alternatives for the currently employed graphite because of their very high theoretical lithium storage capacity (3578 mAh g^{-1} for $Li_{15}Si_4$ and 1623 mAh g^{-1} for $Li_{4.4}Ge$). However, their performance is far from being satisfactory because of the large volume change and severe capacity decay that occurs upon lithium alloying and dealloying processes. To address these problems, we propose and demonstrate a versatile strategy that makes use of the electronic reaction confinement via the synthesis of ultrasmall Ge nanoparticles (10 nm) uniformly confined in a matrix of larger spherical carbon particles ($Ge\subset C$ spheres). This architecture provides free pathways for electron transport and Li^+ diffusion, allowing for the alloying reaction of the Ge nanoparticles. The thickness change of electrodes containing such a material, monitored byan in situ electrochemical dilatometer, is rather limited and reversible, confirming the excellent mechanical integrity of the confined electrode. As a result, these electrodes exhibit high reversible capacity (1310 mAh g^{-1}, 0.1C) and very impressive cycling ability (92% after 1000 cycles at 2C). A prototype device employing such an alloying electrode material in combination with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ offers a high energy density of 250 Wh kg^{-1}.

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New Lithium Recycling Technique of Used Li-ion Batteries using Li Separation Method by Ionic Conductor: LiSMIC

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The world is increasingly turning to the use of Li-ion batteries in electric vehicles; therefore, there is a growing need for lithium (Li). I propose new method for recovering Li from used Li-ion batteries by using Li separation method by ionic conductor; LiSMIC [1]. Li ionic conductor is functioned as a Li separation membrane. This innovative LiSMIC involves the use of an Li separation membrane whereby only Li ions in a solution of used Li-ion batteries permeate from the positive electrode side to the negative electrode side during electrodialysis; the other ions, including Co, Al, and F, do not permeate the membrane.

$Li_{0.29}La_{0.5}7TiO_3$ was selected as the Li separation membrane. The positive side of the dialysis cell was filled with used Li-ion battery solution, and then the negative side was filled with distilled water. In this study, the platinum (Pt) electrodes are bonded to the right and left faces (the two main faces) of the LISM, respectively. The applied dialysis voltage was 5 V, and the electrode area was 16 cm^2 and 4 cm^2 as new Li separation membrane. The Li recovery ratio increased with electrodialysis time. Furthermore, Li permeation speed was not depended on the electrode area, and I succeeded in the development of new Li separation membrane with small area electrode.

After electrodialysis, the Li recovery water was bubbled by CO_2 gas to produce lithium carbonate (Li_2CO_3) as a raw material for Li-ion batteries. The high purity Li_2CO_3 powder was easily generated under CO_2 gas bubbling method. Also, the Li recovery water was dried to produce lithium hydroxide (LiOH) as a raw material for Li-ion batteries. The high purity LiOH powder was easily generated under vacuum drying atmosphere.

Thus, LiSMIC is most suitable for the Li recycling of used Li-ion batteries (Fig.1).

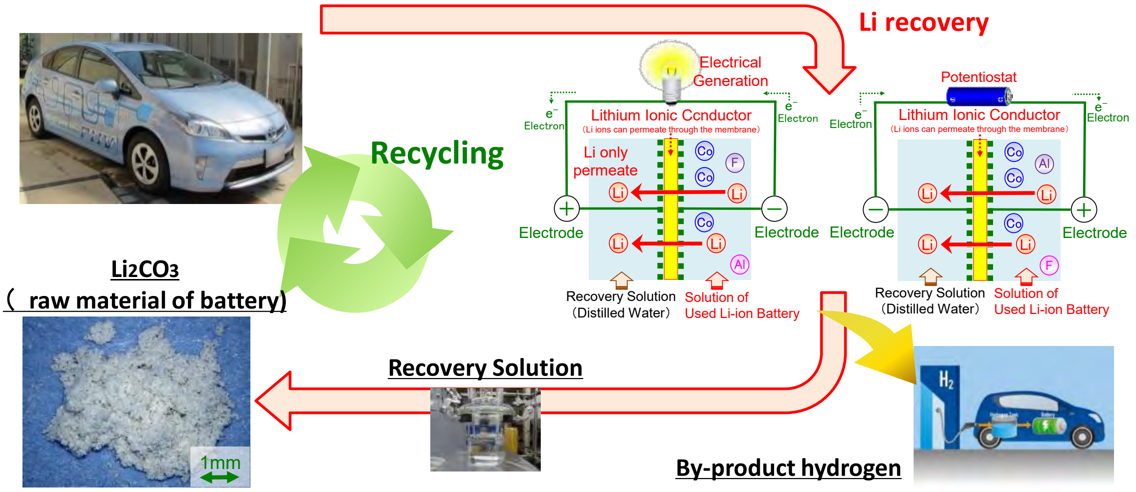

Fig.1 This schematic draw is Li recovery Technology from used Li-ion battery solution using Li separation method by ionic Conductor; LiSMIC. Lithium carbonate (Li_2CO_3) as a raw material for Li-ion batteries is produced from Li recovery solution. And then, H_2 gas is generated as a by-product on the Li recovery side.

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Bioelectrocatalysis for Electrosynthesis

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Electrosynthesis of commodity and fine chemicals is an emerging area. Bioelectrocatalysis has only recently been considered for this application. This talk will discuss the advantages of bioelectrocatalysis for electrosynthesis with examples ranging from ammonia production to pharmaceutical products and intermediates. In the last 5 years, there have been extensive studies and new materials designed for catalytic reduction of nitrogen to ammonia. This is a challenging reductive transformation for traditional electrocatalysts and photocatalysts, but nature can provide an inspiration. Nitrogenase is the only enzyme known to reduce nitrogen to ammonia. This talk will discuss electroanalytical techniques for studying nitrogenase electrochemistry, including both mediated bioelectrocatalysis and direct bioelectrocatalysis. Then, this talk will discuss electrode materials innovation for interfacing these complex proteins with electrode surfaces as well as using them for electrosynthesis of ammonia as well as other value-added products (i.e. chiral amines, chiral amino acids, etc.). Finally, this talk will discuss the use of enzyme cascades for enzymatic bioelectrosynthesis and synthetic biology for microbial bioelectrosynthesis of ammonia and other value-added products.

Electrochemical systems for the treatment of contaminated water: limitations, challenges and prospective

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To minimize the effects of water pollution and alleviate water scarcity, urban water infrastructure will have to be re-invented through implementation of innovative low-cost, energy efficient decentralized water and wastewater treatment systems, and use of alternative water resources. Distributed treatment systems need to be compact, highly efficient, cost-effective, sustainable, robust and autonomous. Among the available technologies, electrochemical systems have the most potential to be used for decentralized treatment of (waste)water. Electrochemical systems do not use chemical reagents, do not form a residual waste stream, operate at ambient temperature and pressure, are robust, versatile and have a small footprint. Yet, to advance from laboratory experiments to practical implementation, there are two key, long-standing challenges that need to be addressed: *1)* high energy consumption and cost; given that most contaminants are present at low concentrations, their electrochemical reactivity in the conventional flow-by two-dimensional (2D) electrochemical reactors is subject to pronounced mass transfer limitations, and *2)* formation of toxic halogenated byproducts in the presence of halides. Three-dimensional (3D) reactor design is characterized by the high electrode surface area to reactor volume ratio and significantly improved reactor efficiency, with a larger effective surface area available for electrolytic degradation of contaminants and reduced mass transfer limitations. Yet, low electrocatalytic efficiency and stability, and high cost of electrode materials are hampering the implementation of 3D electrochemical systems.

In the scope of the ERC Starting Grant ELECTRON4WATER, we are developing 3D electrode materials based on low-cost synthesis process, which are tailored for different water treatment applications (e.g, removal of sulfide from wastewater, removal of perfluorinated compounds from groundwater, removal of persistent organic contaminants from wastewater). For example, Mn-oxide based electrodes were developed for selective and reversible oxidation of sulfide from wastewater to sulfur (Sergienko et al, 2020, Appl. Cat. B Environ.). Although Mn oxide-coated electrodes have been extensively investigated and applied in batteries, this study is the first one to employ Mn-based nanostructured material for electrochemical wastewater treatment. We have also developed graphene-based sponge materials for their use as both cathodes and anodes in small, one-pass, flow-through electrochemical filter units that can treat even low conductivity water (e.g., drinking water) (Pires et al, ACS Nano, submitted). One major advantage of the developed graphene sponges is that they do not produce chlorine, chlorate or perchlorate, while oxidizing the persistent contaminants present at trace concentrations in the water. Thus, this material overcomes one major limitation of electrochemical systems – production of toxic chlorinated byproducts in the presence of chloride, and thus has the potential to strongly influence future research on novel electrode materials for electrochemical water treatment.

While nanostructured carbon- and meta-based electrode materials have been the primary research interest across many fields of material science, such as supercapacitors, batteries, solar cells, and sensors, they haven´t been explored as much for environmental applications. In the ELECTRON4WATER project, we are conducting interdisciplinary research and using the findings achieved in other fields of science to contribute towards further development of electrochemical water treatment systems and their application in a wider scale.

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Designing Quinone-based Conducting Redox Polymers specifically for Aqueous Proton Batteries and for Lithium Ion Battery Cathodes

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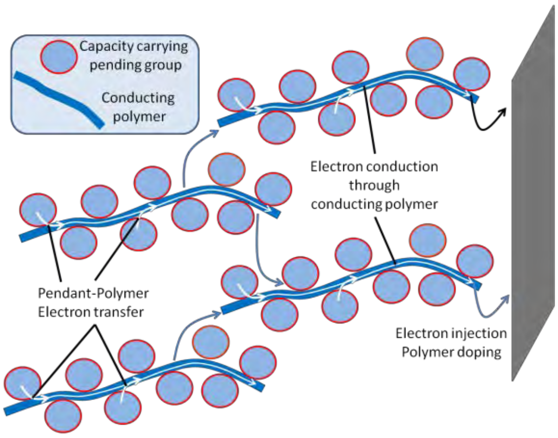
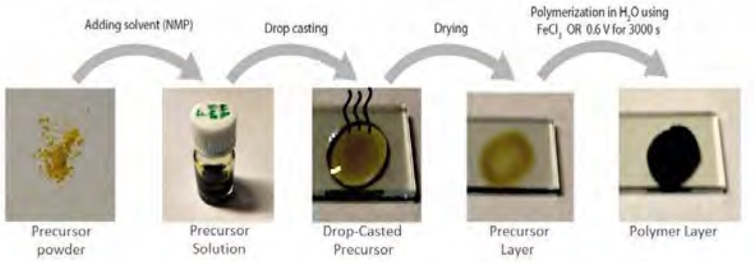


Conducting redox polymers (CRPs) are conducting polymers that have been decorated with redox active functional groups and they provide an attractive alternative as organic matter based electrical energy storage materials. The purpose of the polymer backbone is two-fold, 1) it prevents dissolution of the redox group and, 2) it renders the material conductive. The redox active pendant groups, on the other hand, provide the material with a well-defined redox reaction as well as a high charge storage capacity. CRPs thus provide a solution to two of the most significant obstacles in achieving powerful and stable battery materials from organic compounds, i.e. materials dissolution and limited electronic conductivity while simultaneously providing a high charge storage capacity. For battery applications it is thus essential that the individual properties of the conducting polymer backbone and the redox group can be preserved and that they operate in synergy in the CRP. One prerequisite for synergetic polymer-pendant combinations is redox matching. As conducting polymers are only conducting in their charged state successful combinations rely on that the pendant group has a redox potential within the conducting region of the polymer backbone. In addition, the CRP must allow mass transport of ions, not only related to the cycling chemistry of the pendant group but also ions related to the doping of the polymer backbone. These requirements put significantly different demands on the polymer design for the development of aqueous proton batteries and for CRPs for lithium cycling cathodes. In this presentation specific CRP design-solutions will be presented that allow for the development of all-organic proton batteries [1,2] and for lithium ion CRP-battery cathodes [3].



In addition, a solution-processing method, termed Post Deposition Polymerization (PDP), for CRP-materials and the underlying principles and requirements for PDP will be presented. Importantly, in PDP the processing step occurs prior to polymerization. After depositing and drying of the repeat-unit precursor onto a substrate polymerization is achieved by oxidative polymerization of the precursor. The PDP-method opens up for a scalable method for the coating of CRP materials onto any substrate and can, for instance, be used to make nanostructured CRP materials.

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Elimination of Fluorination: The Influence of Fluorine-Free Electrolytes on the Performance of Si-based Li-ion Batteries

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Eliminating fluorinated electrolytes, susceptible to release toxic and corrosive compounds such as HF, is one step towards more environmentally friendly and safer batteries. Yet, fluorine-containing electrolytes are often considered necessary for enhanced battery performance.[1] Alternatively, replacing the state-of-the-art $LiPF_6$ with fluorine-free salt would reduce cost, increase safety and decrease toxicity, both in the manufacturing and recycling processes.[2] Furthermore, additives in the electrolyte needed to form a stable solid-electrolyte interphase (SEI) are another common source of fluorine, for example fluoroethylene carbonate (FEC), which is particularly important for silicon-based electrodes as they suffer high volume changes upon cycling.[3]

Herein, we investigate the effects of electrolyte fluorination for full cells combining silicon-graphite composite electrodes with $LiNi_xMn_yCo_zO_2$ cathodes, by means of electrochemical testing and post-mortem analysis. The fluorine-free electrolyte is based on lithium bis(oxalato)borate (LiBOB) salt and vinylene carbonate (VC) as SEI-forming additive, while the fluorinated electrolyte is based on the conventional $LiPF_6$ salt with FEC and VC additives. Our results show that although the SEI composition on the anode is very different, both electrolyte formulations are able to stabilise silicon-based electrodes and support stable cycling in full cells (Figure 1). Therefore, fluorine-free alternatives are good candidates for high-energy-density full cells opening new possibilities towards safer, more sustainable and less toxic batteries.

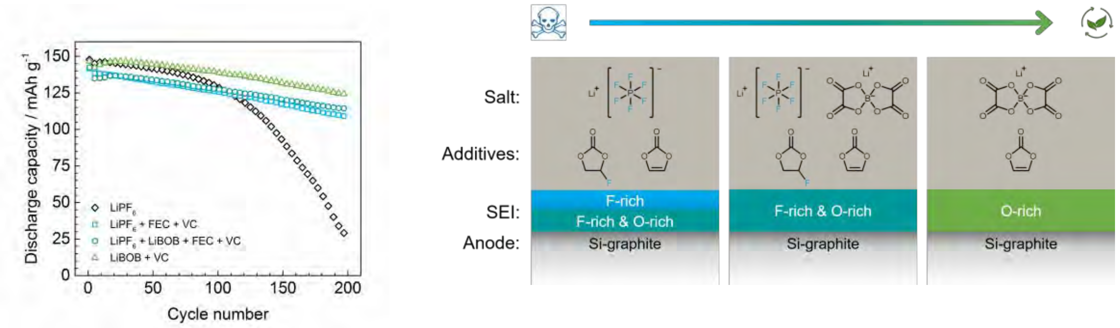

Figure 1. (Left) Discharge capacity of full cells containing different electrolytes: $LiPF_6$ (black rhombi), $LiPF_6$ with FEC and VC additives (blue square), $LiPF_6$ and LiBOB with FEC and VC additives (teal circles), and LiBOB with VC additive (green triangles); and (right) schematic representation of cell constituents and SEI composition.

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Application of Ionic Rectification for Water Purification: Desalination with a Nafion Cationic Diode

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Abstract

Cationic diodes based on Nafion ionomer coated microhole array substrates are combined with an anion conducting membrane to give an AC-electricity driven desalination or salination system. The combination of cationic diode with anionic resistor allows a 3D-printed four-chamber system to be configured with two internal chambers to extract and/or accumulate salt. Three configurations are demonstrated combining desalination and salination for an aqueous 250 mM NaCl solution. For a proof-of-concept device, 50% desalination/salination is demonstrated. The charge efficiency is estimated to be only 12%, limited mainly due to (i) resistivity lowering rectification, (ii) rectification ratio limitations for the array of microholes, (iii) insufficient stability of ionomer membranes under AC-pulse-driven operation. Perspectives for improvements and for future desalination/salination applications are given.

Reconstitution of *Escherichia coli* ATP-Synthase on Gold Electrodes for Potentiometric Detection of ATP

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Modification of electrode surfaces with floating phospholipid bilayers as biomimetic membranes allows reconstitution of membrane-bound enzymes on a controlled way for electrochemical applications. In this way, the catalytic activity of the enzymes associated to transport processes across the biomimetic membrane is combined with the sensitivity of electrochemical detection [1-3].

We report a potentiometric biosensor based on ATP-synthase from *Escherichia coli* reconstituted in a floating phospholipid bilayer over gold electrodes modified with a 4-aminothiophenol self-assembled monolayer. The use of a pH-dependent redox probe on the electrode surface allows a simple, specific and reliable on site determination of adenosine triphosphate (ATP) concentration from 1 μM to 1 mM. ATP is a key molecule as energy vector for living organisms, therefore its detection reveals the presence of microbial colonies. Environments where the existence of microbial pathogens suppose a health hazard can benefit from real time monitoring of such molecule. The broad range ATP biosensor can offer an alternative way of measuring in a few minutes the presence of microbial contamination [4].

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Lubricin, an Antifouling Coating for Electroactive Surfaces

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Electroactive surfaces are a significant component in numerous biomedical applications, such as biosensors and implantable devices used as bionic neural interfaces or controlled drug release platforms. The performance and charge transfer efficiency of electrode surfaces, however, can be significantly affected by the fouling caused by non-specific adsorption of proteins at the surface. These adsorbed proteins act both as a passivation layer and an anchoring point for the further attachment of cells. Likewise, the grafting of traditional anti-adhesive coatings to electrode surfaces, typically charge-neutral polymers such as polyethylene glycol or dextran, often lead to the same electrical passivation effects as the proteins they are protecting against[1].

Conductive polymers (CPs) are an attractive material for sensors and neural interface applications due to their high impedance, ionic and electric conductivity, mechanical softness, and actuation response to applied voltages enabling controlled drug release[2]. Unfortunately, CP surfaces are particularly prone to protein fouling when exposed to biological fluids (e.g. blood, perilymph, saliva) leading to compromised performance and shortened working lifespans[3].

In this work, the issue of fouling is addressed by using lubricin (LUB). LUB, a self-assembling glycoprotein and major biolubricant molecules[4] presents promising properties for use as an anti-fouling agent on bionic electrodes. This includes inherent biocompatibility, protein and cell adhesion resistance. LUB coatings have recently been shown to prevent fouling of platinum, gold, and carbon electrodes with minimal impact on electrode electrochemical activity (i.e. passivation)[5,6]. Notably, this work explores the application of LUB with electrochemically grown polypyrrole (PPy) electrodes and investigates several fabrication methods for incorporating LUB into the polymer structure. The PPy/LUB film structures were characterized along with its electrochemical and fouling resistance properties to assess its ability to protect electrode surfaces against the detrimental effects of biofouling in highly concentrates solutions of proteins and bodily fluids such as blood. Electrochemical characterization using $K_3[Fe(CN)_6]$ as redox reporter (Figure 1) suggested that the optimized LUB-coated conductive films exhibited anti-adhesive properties in fouling solutions. These results reveal the potential application of PPy/LUB film for bionic implant application.

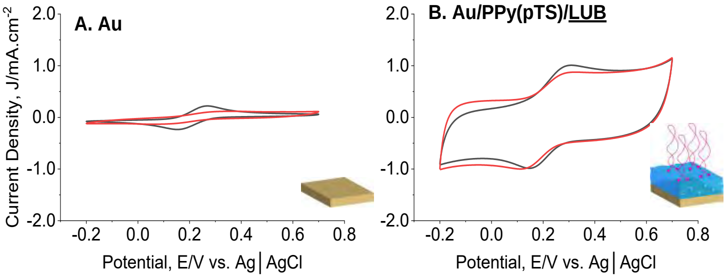

Figure 1: Cyclic voltammograms measured using a scan rate of 100 mV/s and coated gold WE of the oxidation-reduction of a 3.6×10^{-3} mM solution of $K_3[Fe(CN)_6]$ prepared in a nonfouling PBS solution before (black line) and after 2 hours (red line) incubation of BSA protein (5 mg/mL) for a bare gold electrode and a PPy(pTS) and LUB-coated gold electrode. The cycle is the last of 25 cycles

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Electrochemical Sensors Compatible with the Point-of-Care Enabled by Lubricin Antifouling Coatings

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Glucose meters are medical devices that demonstrates the enormous potentiality of electrochemical sensors to operate in whole blood and other biological fluids. Nonetheless, the success of these medical devices has not yet been extended for many other biomarkers.[1] The main impediment to this technology is the nonspecific adsorption of biomolecules such as proteins or even whole cells, which leads to surface biofouling. Biofouling, in the case of electrochemical sensors, may cause a reduction in sensor selectivity by interfering with the interaction of target species with the electrodes surface, or may result in variations in sensor sensitivity by hindering electrode transfer pathway of redox active species.[2] This ultimately leads to sensors failure. In the case of glucose sensing, this issue could be resolved by using semi-permeable membranes that are permeable for glucose (as it is a small molecule) but halt proteins from reaching the sensor surface.[1] Nevertheless, a large number of clinically appropriate biomarkers are the same as the fouling species (i.e. proteins), hence semi-permeable membranes cannot be applied. Additionally, semi-permeable membranes are also themselves prone to fouling, reducing hence their transport properties. Therefore, a major issue to electrochemical sensing platforms that needs to function in biological fluids remains the biofouling of electrode surface. This highlights the need for development of sensor surfaces that can function in complex biological fluids for the analytical detection of biomarkers.

Here, we report the use of lubricin (LUB) in response to the biofouling issue. LUB is a cytoprotective glycoprotein present in synovial fluids and coating cartilage surfaces in articular joints.[3] LUB displays a distinguishing chemistry, conformational and molecular structure, and also the ability of self-assembling in a well-organized manner on substrates from different nature.[4] When attached to a conductive surface, LUB presents the capability of preventing biofouling and at the same time allows good electrochemistry with the advantage of a simple and one-step coating preparation.[5] This makes LUB an interesting surface coating for electrochemical biosensing. In this work, the detection of electroactive species, benzodiazepines, is reported. The prepared electrodes showed a good analytical response in biological fluids such as saliva and whole blood, being able to detect very low concentrations (as low as picomolar) of the investigated analytes. Square wave voltammetry was used as excitation technique for the quantification. In these sensors, LUB works as both, antifouling agent as well as an active component for the analyte detection. Aiming the compatibility with the point-of-care, reduced graphene screen-printed electrodes was used as a substrate to the LUB functionalization (Figure 1).

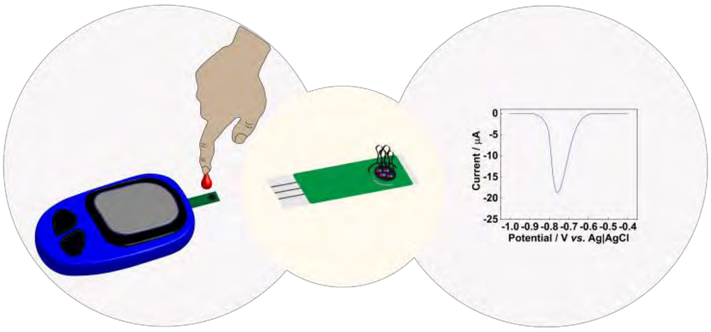

Figure 1 – Schematic representation of the sensing platform. LUB is self-assembled on a reduced graphene oxide to allow the detection of electroactive species in biological fluids. The excitation technique used for measurements is square wave voltammetry.

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Toward the definition of new hybrid proton exchange membranes for PEMFC: from NMR molecular dynamic studies to electrochemical performances

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Highly hydrophilic nanostructures, most of them layered-type (smectite clays, layered doubled hydroxide-LDH, graphene oxide-GO), have been properly synthesized and organo-functionalized to interact with a ionomer in order to prepare advanced nanocomposite membranes for PEMFC applications. As nanofillers in Nafion® polymer, they can modulate the nature of water confined in the nanosized ionic channels with the result that the hybrid membranes show high proton mobility in dehydrating state. Additionally, many efforts are devoted in the development of alternative ionomers to commercial Nafion, based on non-fluorinated macromolecules with adequate mechanical strength, high proton conductivity and stability in the aggressive environment of a working fuel cell. Studies on hybrid membranes based on sulfonated Polyethersulphone (PES) and Polysulfone (PSU) will be presented.[1,2]

The 2D nanofillers of interest are those with a layer-like morphology characterized by a high aspect ratio (large lateral dimensions and small thickness), and hydrophilic functional groups on the surface in order to provide more sites for the coordination of water molecules and to build long-range proton transfer pathways inside the membrane.

LDHs and smectite clays are anionic and cationic minerals, respectively, with a unique combination of swelling, intercalation and ion exchange properties. Appropriate organo-functionalizations by using simple chemical methods with organic/inorganic guest molecules have been operated. Noteworthy is a hybrid material obtained by rooting CNTs (decorated with RSO3H groups) on smectite plates, providing an outstanding effect on the protons transport in the nanocomposite membrane due to the formation of an appropriate network which favors the Ghrotthus-type mechanism.[3]

Graphene Oxide (GO) is characterized by the presence of oxygen–containing moieties, mostly hydroxyl, epoxy and carboxyl groups on the carbon sheets. Organo-modified GO was synthetized and tested as nanofiller for the creation of novel hybrid nanocomposites with enhanced proton transport.[4]

The barrier property of such 2D-materials was also valuated to reduce the methanol crossover (critical issue in the DMFCs). The exfoliation and dispersion of the layers throughout the continuous polymeric matrix can significantly increase the tortuosity of the methanol's diffusion path. Moreover, a higher order's degree in the arrangement of the filler's platelets, e.g. aligned parallel to the membrane surface, may further reduce the detrimental effect of the methanol permeation as a consequence of the greater obstruction and increased tortuosity of the fuel diffusion path.

With this aim, a mechanical alignment of GO and LDH lamellae within the polymer matrix has been attempted and anevidence of lamellae's alignment at the nanoscale was obtained through the Magnetic Resonance Imaging combined with Rheology (Rheo-MRI) technique, an effective and elegant method, as well as original for such investigations, to study the organization of nano-lamellae dispersed in a polymeric solution under the shearing.[5,6]

NMR was widely used to investigate molecular dynamics through direct measurements of self-diffusion coefficients (Pulse Field Gradient–PFG technique), relaxation times (T_1 and T_2) and spectral analysis, in order to achieve a systematic understanding at a fundamental level of the effects of dimensionality and organization of these nanofillers on the physico-chemical, mechanical and electrochemical properties of the membrane electrolytes.

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Local Electrochemical Measurement with 3D Printed Solution Flow-type Microdroplet Cell

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Metal materials are widely used and have advanced properties, such as high strength, high corrosion resistance and flatness. Non-uniformity of materials play an important role in these properties. In order to investigate the non-uniformity, it is necessary to perform a higher resolution analysis. Therefore, electrochemical technology in a small area is required. One of the techniques is a electrochemical micro-cell. The electrochemical micro-cell has been attracting attention as a measurement method on a small surface area. The Electrochemical micro-cells are classified into two types, a meniscus type and a gasket type, due to the difference in the structure of the capillary tip and the sample electrode[1), 2)]. These two types of electrochemical micro-cells have enabled us to investigate small surface area. However, in these two types, when intense electrode reaction occurs, the change in the solution concentration near the sample surface becomes remarkable. In this case, a concentration gradient is generated in the solution inside the capillary, so appropriate measurement and chemical reaction cannot be performed. To solve this problem, Lohrengel et al. developed a gasket-type electrochemical micro-cell with a θ-shaped glass capillary[3)]. Solution supply and ejection could be performed using two channels. Fushimi et al. developed a dual capillary solution flow-type microdroplet cell (Sf-MDC)[4)]. It has a coaxial double tube structure in which two capillaries with different diameters are combined, the solution is supplied from the inner capillary, and the solution is collected by the outer capillary. Using Sf-MDC, Sakairi et al. controlled the area and thickness of porous-type aluminum anodic oxide[5), 6)]. Hashizume et. al. investigated SCC mechanism near fusion line by Sf-MDC[7)]. This Sf-MDC is very useful for various area selective electrochemistry applications. However, the structures of previous Sf-MDC are very complex and difficult to fabricate. Therefore, in this study, 3D printing was applied to fabricate Sf-MDC and local electrochemical measurements were carried out by fabricated Sf-MDC.

Sf-MDC was designed using computer-aided design software and fabricated by 3D printer. A platinum wire and an Ag / AgCl wire were inserted inside the cell as counter and reference electrodes. The cell equipped with the electrodes was attached to a microscope (Fig. 1). Using this setup, it was possible to control precisely the measuring position and carry out the area selective electrochemistry.

The surface state before and after the electrochemical measurements was observed, and the immersion potential measurements and the electrokinetic polarization measurements were performed on materials using 10 mM NaCl. The immersion potential and the polarization curves of aluminum alloys were observed. The obtained curves showed fluctuations, depending on the material location.

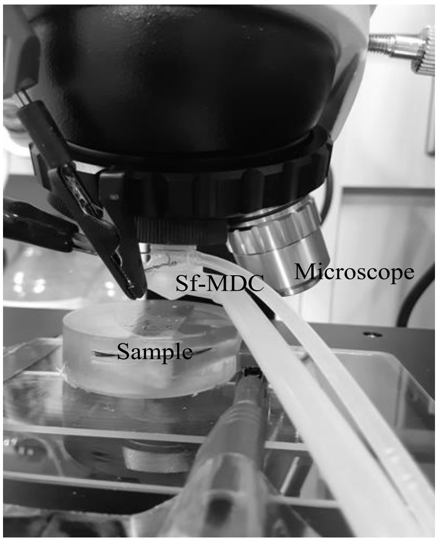

Fig. 1 Sf-MDC fabricated by 3D printer attached to optical microscope.

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DNA/carbon-based super lattice electro active hierarchical self-assembled nano networke for biomedical detection and bio sensing

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In this study, a new effective and DNA and DNA like polymer based self-assembled and hierarchical nanostructures was designed that can be used for bio sensing applications. SWNT-DNA hybrid Nano structure fabricates by region selective covalent combined between DNA and SWNT Nano particles These hybrid Nano structures have different electrochemical properties compare of alone SWNT and DNA single strand. Electrochemical behavior of SWNT-DNA hybrid Nano structures are studied by cyclic voltammetry and impedance spectroscopy technique. Due to wire shape SWNT-DNA hybrid Nano structures have favorable electrical properties could be used in fabrication of genomic biosensor which was detected mismatch and abnormality in ds-DNA. In other attempt, a three-dimensional (3D) hierarchical architecture for aerographite bio electrodes was fabricated by template-directed self-assembly. The superlight aerographite was functionalised with guanine (G) rich polymer loaded with glucose oxidase (GOx) thorough π-π interactions of electron pairs of the guanine ring and the electron cloud of aerographite. These superlight and hierarchical graphene based nanostructure detected glucose in solution with satisfy sensitivity.

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Sensing possibilities of diferrocenylborinic acid immobilized in 2D-titanate nanosheet host

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The diferrocenylborinic acid (Fc_2BOH) contains two interconnected and communicating redox centres. The boron bridge between two ferrocenyls is able to interact with other analytes as nucleophiles, diols etc. [1] The main aim of our work was to describe the fundamental electrochemical behaviour of such system with two redox centres in relation to model analytes as fluoride. We also wanted to widen knowledge about intramolecular communication between joint redox centres.

Fc_2BOH has been synthesized in good yield *via* an improved synthetic path. Its physicochemical characterisation was carried out using NMR, HRMS, FTIR, X-ray crystallography, and then by electrochemical methods. These revealed the desired two one-electron oxidation processes for the two electronically coupled ferrocenyl moieties. The redox properties of Fc_2BOH in homogenous phase (organic media) was contrasted to those in heterogeneous phase. For this purpose, a new concept of modification of electrode recently developed by Marken's group [2] has been utilized – Fc_2BOH was incorporated into a lamellar film of 2D titanate nanosheets on a glassy carbon electrode. Data from cyclic voltammetry and from square wave voltammetry confirmed that the bridging boron can bind to nucleophiles (hydroxide, fluoride) upon oxidation of the ferrocenyl groups.

An immobilization in 2D-titanate nanosheet film has proven as a good modification technique as these were successfully employed to host Fc_2BOH on a glassy carbon electrode. In the presence of disodium sulphate in aqueous electrolyte, a stable reversible voltammetric response was observed. In the presence of sodium fluoride, "bound" and "unbound" states of Fc_2BOH were observed at higher scan rates (above 0.1 Vs^{-1}). Mechanism of interaction has been proposed and discussed and sensing applications suggested.

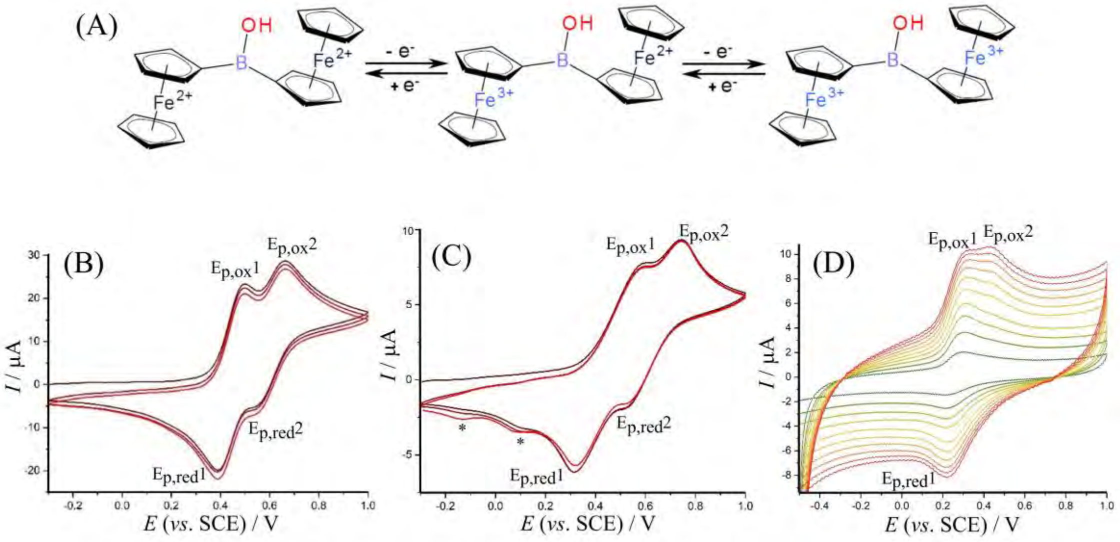

Figure: Redox properties of Fc_2BOH (A) in homogenous (B – in acetonitrile, C – in dichloromethane) and heterogeneous phase (D – immobilized in 2D-titanate nanosheets).

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Modified Hydrocyclone as Electrochemical Reactor: Modelling, Characterization and Applications

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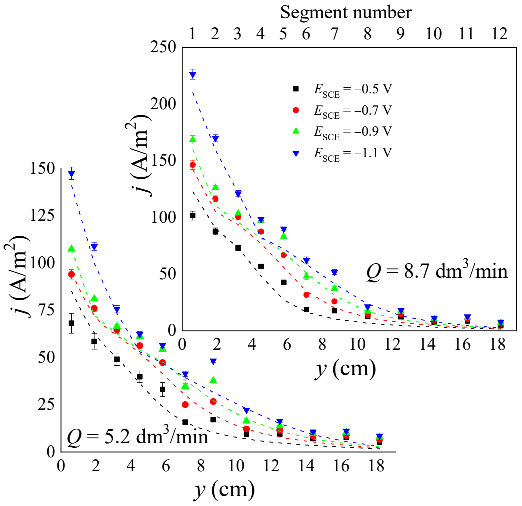
Many electrochemical industrial processes take place under a mixed kinetic control, such as: electrochemical wastewater treatment or inorganic-organic electrosynthesis. These situations demand for extensive research efforts in order to develop electrochemical reactors with good mass-transfer conditions. Thus, it is pretended to maximise the space time yield of the reactor and to become more uniform its potential distribution with the aim of to avoid, as much as possible, the presence of secondary reactions or electrode degradation.

Hydrocyclones are often used in the chemical industry when different phases need to be separated. These devices are characterised by their constructive easy, without moving parts, and simple operation. The double helical flow existing in the interior of a hydrocyclone suggests improved mass-transfer conditions. Thus, it has been proposed as an electrochemical reactor,[1] being the cylindrical-conical casing operated as working electrode whereas the counter electrode is placed at the overflow. The proposal has two additional aspects: (i) if a solid is produced at the working electrode, depending on particle size, it can be separated from the spigot and (ii) the hydrocyclone shows a low-pressure region in its central part, known as air core, which becomes appropriate for the introduction of a gas phase. Therefore, it can be considered as an alternative reactor for a two-phase operation.

In this work, a mathematical model to calculate tertiary current distributions in electrochemical reactors is presented taking into account the potential and concentration fields together with the hydrodynamics under laminar or turbulent conditions. Multiple reactions with different kinetic controls are considered at both electrodes. The computational algorithm solving the model was implemented in OpenFOAM.



The model was validated by using some test reactions from dilute solutions employing a supporting electrolyte,[2] but also without it in order to study the effect of ionic migration. The experiments were carried out in a modified hydrocyclone with a segmented cathode, 12 segments. A close agreement between experimental and predicted current distributions was obtained as it can be concluded from the figure on the left-hand side, which compares theoretical, dashed lines, and experimental, points, current distributions for different values of both volumetric flow rate and applied cathodic potential. In the figure, the test reaction was ferricyanide reduction.

The modified hydrocyclone was also examined as an alternative reactor for the electrochemical processing of two-phase systems. Experimental measurements demonstrate an appropriate hydrodynamics of the equipment. Mass-transfer measurements corroborate the good performance of the cylindrical body of the hydrocyclone. Copper electrodeposition[3] and sulphur dioxide reduction to colloidal sulphur[4] were used to check the behaviour of the reactor, being it promising for these tasks.

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New tools for the rational development of metal-sulfur batteries

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Metal-sulfur batteries have an outstanding theoretical specific energy, but their development is hampered by their complicated and not fully understood reaction mechanisms, in which a variety of polysulfide species are formed in the pathway of the reduction of sulfur to metal sulfide. Performance improvements can be obtained by tuning the electrolyte properties, e.g., in terms of polysulfide solubility/speciation. Consequently, in order to guide a rational method for electrolyte optimization, we have developed a reliable analytical method that enables the determination of the total solubility of polysulfide species and the average chain length of polysulfide species in the polysulfide solutions, which are key properties that critically affect battery performance and, in particular, the role of polysulfide species as intermediate species [1].

However, the performance of metal-sulfur batteries is also critically affected by the interplay between electrolyte formulation and electrode composition. To study such effects, we have recently demonstrated the use of a simple impedance-based method of analysis of porous electrodes, using a transmission line model with only two fitting parameters, to quantify the rate of ion transport within the porous electrode, which we have shown is a key property determining the electrode performance [2,3]. Figure 1 illustrates the physical meaning of the model, with electrons travelling through the carbon conductive additive (in **black**) and ions (e.g., Li$^+$) travelling through the electrolyte filling the pores (in **blue**). Interestingly, we found that the electrode/electrolyte combinations that resulted in faster ion transport were also the ones leading to optimal battery performance, thus providing the bases for the rational design of high-performance batteries.

For the direct detection of polysulfide species formed during the operation of metal-sulfur cells, we have also developed a novel cell design incorporating a reliable and highly sensitive electrochemical sensor. With the use of a glassy carbon sensor material, the detection of polysulfides is achieved with unprecedented sensitivity [4,5].

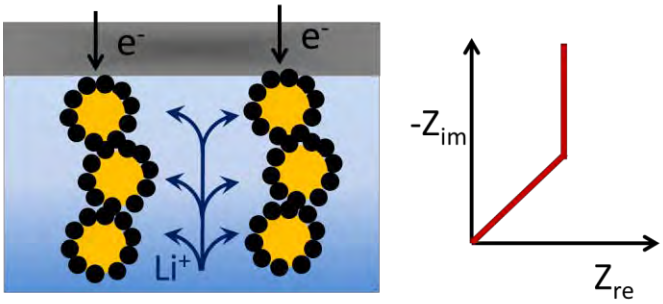

Figure 1. Illustration of the meaning of the transmission line model used to characterize sulfur-carbon composites for Li-S battery applications and Nyquist plot of the associated impedance spectrum.

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Two steps synthesis of D-glucaric acid by electrocatalytic oxidation of D-glucose on a gold electrode: influence of operational parameters

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The ambition to convert our fossil-fuel economy into a decarbonized economy will inevitably pass through the use of renewable energy platforms, such as wind, water, sun and nuclear fission. Similarly, also the production of chemicals is meant to reduce its dependence on a petroleum based feedstock, promoting instead the use of bio-waste (up to 138 million tons per year in the European Union [1]), which seemly fits in the concept of circular economy. The selective oxidation of glucose to gluconic acid, and its subsequent oxidation to glucaric acid are potentially key steps in the biomass-to-chemicals value chain for the numerous application of glucaric acid, for example, in the production of metal complexation agents, biodegradable polymers and detergents [2]. Nowadays the major challenge for the bio-based chemical production of glucaric acid is the lack of a suitable conversion technology [3]. Especially when compared to the already settled petrochemical technologies based on fossil resources, the conversion of renewable carbon to chemicals is the most undeveloped and complicated of all biorefineries [3]. The most promising technique up-to-date is the electrochemical oxidation, which involves the transfer of electrons in the reactions, eliminating the use of high O_2 partial pressure or of hazardous oxidants. Additionally, it can be operated under mild conditions and allows control over the selectivity by tuning the electrode potential. In our recent work we demonstrated the correlation between the oxidation potential and the reactivity of the functional groups of glucose for three selected metal electrodes [4]. The best selectivity to the products of interest was obtained on gold where a low oxidation potential (0.55 V_{RHE}) leads to the selective production of D-gluconic acid, while a more positive potential (1.30 V_{RHE}) promotes the further oxidation to D-glucaric acid [4].

Here, we investigated the impact of the operational parameters (pH, substrate concentration, cell voltage, temperature and reaction time) on the two oxidation steps separately (respectively starting from glucose and gluconic acid) with as final aim to identify those conditions that ensure an optimal selectivity to glucaric acid. Our results show that while the selectivity of the first oxidation step is highly dependent on the pH and temperature of the electrolysis, the second step is mainly affected by the applied potential during the electrolysis experiment. The best selectivity that could be obtained in the first oxidation step to gluconic acid was 97.6%, at 0.55 V_{RHE}, 5°C and pH=11.3; and in the further oxidation to glucaric acid was 89.5% at 1.10 V_{RHE}, 20°C and pH=12.5.

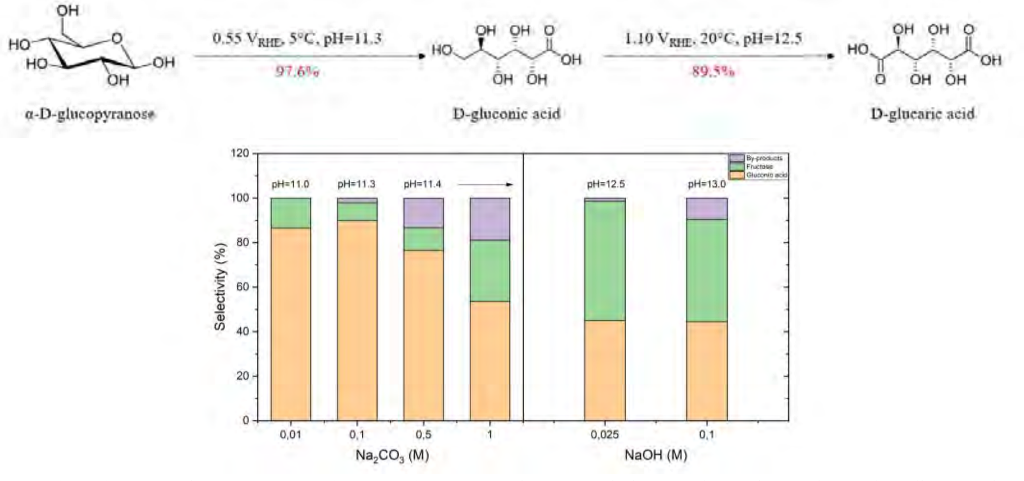

Figure 1: (Top) Reaction scheme, (bottom) change in selectivity as function of pH for first oxidation

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DNAzyme Based Sensor for the Detection of Metal Ions in Solutions Using Resistive Pulse Sensing

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Based on the Coulter counter principle, resistive pulse sensing (RPS) measures particles on a particle by particle basis as they traverse a nanopore providing information on particle size, concentration and charge. RPS has been used to measure a large variety of analytes such as proteins, DNA, and metal ions. The use of DNAzymes for the detection of metal ions has been demonstrated for multiple targets.

Currently most strategies rely on the use of fluorescence to measure the cleavage of DNA upon target metal binding. RPS offers a label free sensing method as it can resolve the changes from ssDNA to dsDNA. Here we develop the use of DNAzymes with RPS technologies for the detection of calcium ions in solution.

We present the initial testing which indicates the ability to measure calcium ions binding with our DNAzyme before the DNA undergoes re arrangement as demonstrated through changes in the particle speed, figure 1b. We demonstrate the change in speed to be proportional to the amount of Ca2+ present, figure 1d, and our assays selectivity over a mixture of other metal ions. The work allows for future development of the assay for environmental testing and the ability to multiplex it previously designed metal ion aptamers.

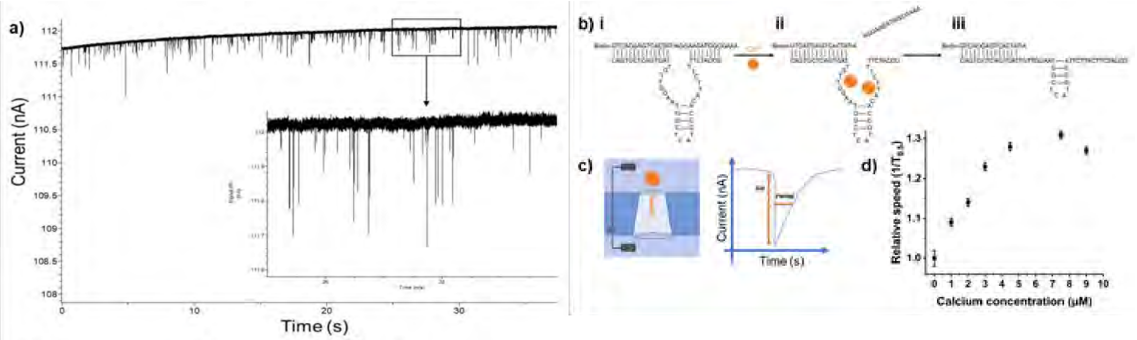
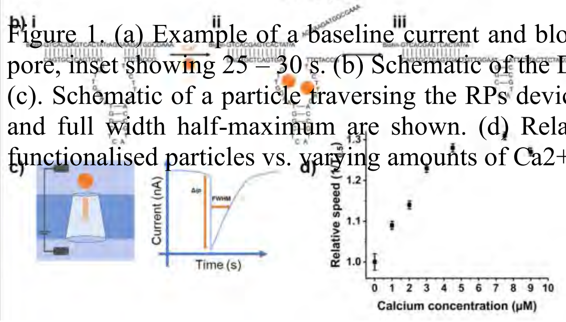


Figure 1. (a) Example of a baseline current and blockade events caused by the carriers translocating the pore, inset showing 25 – 30 s. (b) Schematic of the DNAzyme binding with Ca2+ ions before rearranging. (c). Schematic of a particle traversing the RPs device and the signal produced. Blockade magnitude Δip, and full width half-maximum are shown. (d) Relative particle speeds normalised to blank DNAzyme functionalised particles vs. varying amounts of Ca2+ ions from 1 – 9 µM.



Natural Methylxanthines: Multifacet Starting Materials in Electroorganic Synthesis

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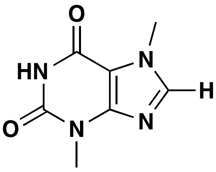
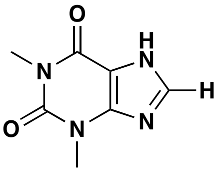
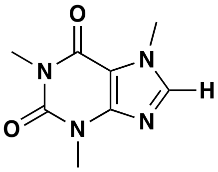
Natural methylxanthines (caffeine, theophylline, theobromine) are abundant natural compounds present in more than 60 plants, cocoa, tea and coffee among the most famous. They can be thus considered renewable bio-based reagents.


Theobromine


Theophylline


Caffeine

Their stucture (uracil and imidazole fused rings) can, in principle, be transformed into many different derivatives, not only by functionalization of the nitrogen atoms, but also by opening of one of the two rings. Nonetheless, methylxanthines are molecules particularly resistant to ring chemical transformations, needing very harsh conditions to open one of the two rings.

In this context, electrochemistry can play an important role as it allows the methylxanthines structure transformation under quite mild conditions.

Although the anodic oxidation of these natural compounds is by far the prevalent electrochemical reaction reported in the literature (and widely used in electrochemical sensors), also their reduction is possible, both in the absence and in the presence of the imidazole nitrogen alkylation prior to the cathodic reduction.

This presentation will deal with the various possibilities to transform theophylline and caffeine by electrochemical means, by both anodic and cathodic reactions, evidencing analogies and differences with the reactivity of the same species carried out by classical chemical reactions.

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Monitoring of Vancomycin and Gentamicin Treatment Using Electrochemical Sensors

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Vancomycin (VAN) is a glycopeptide antibiotic, with bactericidal action towards Gram-positive bacteria, in particular enterococci, streptococci and staphylococci. VAN is indicated parenterally for the treatment of severe infections caused by bacteria resistant to other antibiotics and for the prophylaxis of postoperative infections [1]. Gentamicin (GEN) is an aminoglycoside antibiotic, widely used as prophylaxis and treatment in many clinical situations, like severe infections with a wide range of Gram-negative bacilli, against staphylococci and certain mycobacteria [2]. The treatments with VAN or GEN can lead to ototoxicity, nephrotoxicity and bacterial resistance to antibiotics, needing a therapeutic monitoring of these antibiotics that maximizes efficacy, reduces toxicity and the spread of the antibiotic resistance.

The purpose of this study was the development of fast and sensitive methods for the electrochemical analysis of VAN and GEN from biological samples (human serum and urine).

Two strategies were used for the electrochemical detection of VAN. First, involving a battery of tests, the complex electrochemical fingerprint (CEF) of VAN was achieved, incorporating the electrochemical behavior of VAN at different commercially available screen printed electrodes, at several electrolytes, at successive analyses, after simple pretreatment, using both the anodic and cathodic peaks.

The second method was based on the interaction between VAN and gold. Thus, a hybrid graphene-gold nanostructures electrode was employed for the direct VAN detection by anodic oxidation and for the indirect VAN detection, using the electro-active gold nanostructures as probe to monitor the changes in their cathodic signal due to the interaction between gold nanostructures and VAN.

In order to explain the electrochemical behavior of vancomycin, the mechanism of the VAN anodic oxidation was elucidated by high performance liquid chromatography coupled with mass spectrometry analyses of the products obtained after small scale electrolysis and a two-step electrochemical-chemical mechanism was proposed.

The electrochemical behavior of GEN was studied using different electrochemical techniques, different electrolyte solutions and several screen printed electrodes (SPE): carbon-based (C-SPE), graphene-based (G-SPE), platinum-based (Pt-SPE), gold-based (Au-SPE) and carbon-based modified with gold nanoparticles (AuNP-SPE). A sensitive and selective electrochemical method was developed using the GEN anodic oxidation in alkaline medium at the C-SPE.

To facilitate a fast and simple electrochemical detection of VAN and GEN from human serum and urine, different treatments of the biological samples were tested. The human serum and urine containing Van or GEN were treated with different protein precipitation agents, liquid-liquid extraction and different solid phase extraction procedures and the influence of each treatment on the electrochemical signal of VAN or GEN and of the interferents was tested. Also, the electrochemical analysis of VAN and GEN from human serum and urine was optimized in terms of electrode material, electrolyte and electrochemical technique in order to eliminate/diminish the electrochemical signal of the interferents from these complex matrices.

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Effect of intentional convection on passivation of Fe-6Cr surface in acidic Na_2SO_4 solution

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The anodic oxidation behavior of Fe-6Cr during potentio-dynamic polarization in pH 4.5 Na_2SO_4 solution was investigated by electrochemical ellipso-microscopy. Active, passive, and trans-passive states of the Fe-6Cr surface showed heterogeneous oxidation behaviors depending on the substrate micro-structure, electrode potential and solution convection. Enhancement of mass-transport by solution injection in the latter half of the active state resulted in acceleration of passivation of the Fe-6Cr surface. The passivity-current density of the surface passivated by intentional convection was reduced to almost half of the current density of the surface that had been in the passive state in a stagnant solution, and the surface passivated by intentional convection showed better resistance against pitting in a chloride-containing solution. The improvement of passivity of the surface was attributed to the formation of a Cr-enriched passive film by a decrease in the thickness of the diffusion layer in the latter half of the active state.

Electrochemical imaging of E.coli biofilms using Soft-Probe-Scanning Electrochemical Microscopy

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Biofilms are slimy layers composed of attached microbial cells, which are embedded in a matrix of extracellular polymeric substances providing protective functions. Biofilms secreted by the microbes play a major role in the manifestation of severe infectious diseases. It has been estimated that about 80% of chronic microbial infections in the human body are due to bacterial biofilm formation. Biofilms are of serious universal concern because they provide increased protection against antibiotics, which can be 10-1000 times higher than observed in free-floating cells. They represent also a host defense system against competing microbes and external physical and chemical factors.[1] Biofilms are usually analyzed by using fluorescence imaging, which has limitations because it does not allow long-term observations of different biofilm developmental stages. Here we demonstrate that electrochemical detection is a suitable method to overcome this limitation.

We present electrochemical imaging of *E. coli* biofilm development and long-term monitoring of biofilm metabolic activities using soft-probe scanning electrochemical microscopy (SECM). Soft probes are made of thin flexible insulating plastic films with embedded carbon microelectrode. They are brushed in a gentle contact mode over the biofilm surface guaranteeing a constant working distance while the biofilm remains intact. Biofilms were grown for up to ten days on various substrates including glass, plastics and metals. The oxidized form of redox-active species was reduced by the metabolic activity of the biofilm. This allowed SECM feedback mode imaging (Fig. 1). Finally, the advantages and perspectives of using soft probes towards the potential mapping of metabolic communication molecules in biofilm communities will be discussed. Finally we aim at developing methodologies for using electrochemical methods for the disinfection of bacterial biofilms.

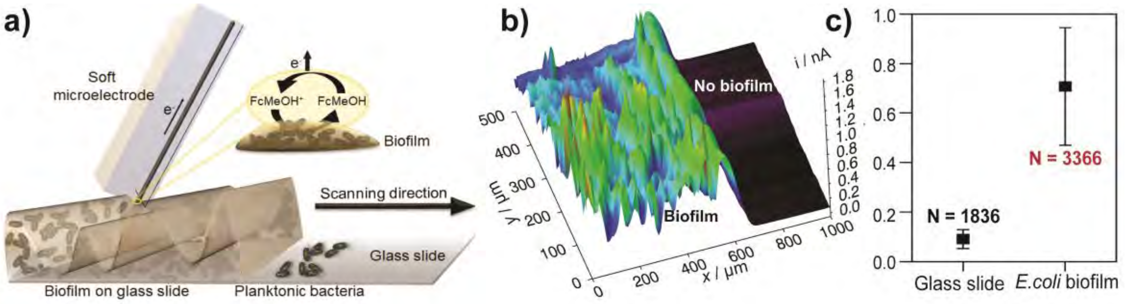

Figure 1. a) Schematic representation of SECM feedback mode imaging of a biofilm using FcMeOH as redox mediator. b) Feedback mode Soft-Probe-SECM image. c) Mean currents ± standard deviation values over the *E.coli* biofilm and bare glass. Experimental details: working potential $E_T = 0.4$ V, probe translation speed = 25 µm/s, step size = 10 µm, 2.5 mM FcMeOH in 100 mM PBS (pH = 7.4).

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Multifunction Nanostructured Coatings for Corrosion Protection. Contribution to a Sustainable Technology

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The active corrosion protection of metallic substrates can be achieved by addition of corrosion inhibitors to protective coatings. However, direct mixing of an inhibitor with coating formulations can lead to important drawbacks decreasing barrier properties of the coating and diminishing activity of the inhibitor. Also, soluble inhibitors can cause phenomena like osmotic blistering or be leached out spontaneously to the environment, which limits long-term performance and is environmentally pernicious. To overcome this problem and have controlled release of inhibitor different strategies of inhibitors storage in nanocontainers have been developed in order to produce smart self-healing coatings. Successful use of this technology could allow the replacement of Cr VI traditionally used in coatings and other surface treatments, as this is a hazardous health and environmental product.

In this work novel protective nanostructured coatings with self-healing ability are presented. This effect is obtained on the basis of nanocontainers that release entrapped corrosion inhibitors in response to local pH changes or presence of corrosive species. The development of new nanocontainers for organic and inorganic green corrosion inhibitors is described, especially the most promising from industrial point of view, based on Layered Double Hydroxides (LDH). The combination of different of these nanocontainers in the same coating system has proved to be effective to accomplish further functions as antifouling and sensing. Potential use of materials that exist in nature will also be reviewed.

Electrochemical Plasmonic Optical Fiber Probe for Real-time Insight into Coreactant Electrochemiluminescence

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Electrochemical surface plasmon resonance (ESPR) is a powerful technique for defining dynamic changes in chemical composition and morphology of functional interfaces by correlating spectral information with voltametric characteristics of the electrode processes.[1, 2] However, conventional Kretschmann prism-based surface plasmon resonance (SPR) configurations require sophisticated apparatus and complex optics. Here, we present a versatile flow injection ESPR device that incorporates a plasmonic and conductive fiber optic probe, for which a gold nanohole array film is integrated onto the endface of a conventional optical fiber via template transfer. The coreactant-based $Ru(bpy)_3^{2+}$ / tripropylamine (TPrA) electrochemiluminescence (ECL) system, is chosen to unravel electrochemically-induced real-time interfacial information, since such an approach is increasingly employed for clinical assay analysis and the associated ECL mechanism is an active area of investigation. The ESPR observations provide novel experimental evidence to support the proposition that ECL reactions undergo an oxidative-reduction pathway. Moreover, the ESPR peak shift exhibits a broader linear detection range of TPrA concentration (0 - 20 mmol L^{-1}), compared to the ECL and SPR techniques. This study clearly demonstrates that the novel fiber optic ESPR device presents as a reliable and multimodal spectroelectrochemical platform to gain mechanistic insights into complicated chemical processes and provide sensing capabilities, while offering great simplicity, portability and miniaturization.

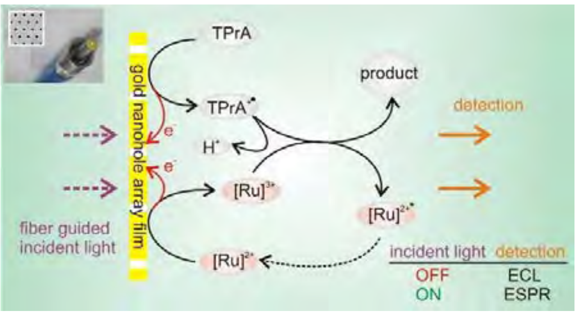

Figure 1. (Top-left) SEM image of the gold hexagonal nanohole array film and optical fiber tip after a gold nanohole film transferred. (Centre) Fiber optic ESPR device, and oxidative-reduction pathway for the coreactant ECL system. (Bottom-right) Multiple modes for signal detection.

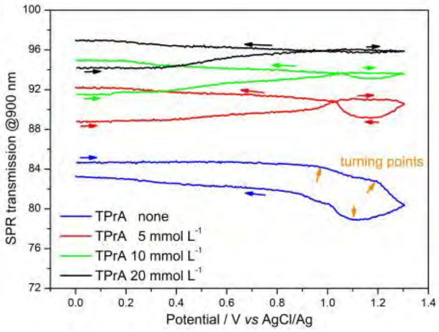

Figure 2. SPR transmission intensities at 900 nm in 1.0 mmol L^{-1} $Ru(bpy)_3Cl_2$ and 0.1 mol L^{-1} PBS (pH = 7.4) solutions containing a varied concentration of TPrA at a scan rate of 50 mV s^{-1}.

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Teaching electrochemistry without Fake News

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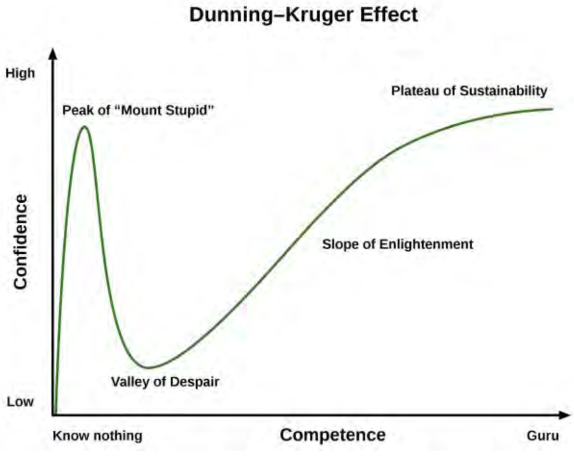
As the teaching support of electrochemical science has moved from textbooks, to slides and on-line information providers, many concepts of electrochemistry have become simplified to the point of becoming totally wrong.
Indeed, a textbook usually took many years of preparation and was thoroughly reviewed. The information was reflecting the knowledge of the time but could generally be trusted. Nowadays, fewer textbooks are published and many teachers gather their teaching material from on-line sources.

Here, we shall review some FAKE NEWS that propagate through the literature and unfortunately to lecture notes.

The most damaging fake news is that of the HOMO-LUMO semantic to express the redox stability of an electrolyte in a battery. It started in a publication from well-known scientists and propagated virally.
Another fake news is again a HOMO-LUMO semantic to express the solvent re-organisation energy in electron transfer theory.
A less damaging fake news consists of saying that the current reaches a maximum in linear sweep voltammetry because the reactant concentration drops to zero at the electrode. This is not the case…
Other fake news are based on an obsolete vocabulary. A classic example is the use of NHE to refer to SHE; indeed, very few are still familiar to the concept of normality in solution chemistry.

Many students find electrochemistry to be a difficult subject in their curricula. Indeed, electrochemical reactions take place at a surface and a basic knowledge in solid state physics and of electrolyte solution chemistry is required to understand interfacial reactions with the difficult concept of electric potentials (so many of them: inner, outer, surface, redox, electrode, Nernst, Donnan, Galvani, Zeta, ..)
In many *cursi*, electrochemistry is not taught any more by physical chemists to physical chemists, but to a much larger audience with a much more disperse background. This requires a rewriting of old concepts in a unified approach. The presenter still wanders where he is on the Dunning-Kruger curve below (Courtesy of Wikipedia), but nonetheless will advocate for the teaching of the Fermi level of the electrons in solution to present electrochemical science in a unified framework.



Development of a European Master Programme Curriculum in Fuel Cell and Hydrogen Science and Engineering

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Hydrogen related technologies, like *e.g.* fuel cells and water electrolysis, are currently rapidly progressing to reach full market application. This fact is indicated by an exponentially growing number and size of demonstration activities, as well as by growing interest on side of the industry. Motivation for this trend clearly follows from the policy of reduction of CO_2 emissions, as well as dependence on the politically instable regions exporting fossil fuels. It is, however, necessary to keep in mind the important aspect that hydrogen technologies, as a typical representative of novel hi-tech processes, depends very significantly on the availability of correspondingly trained operators, not mentioning development, production and installation teams. For the moment, preparation of respective staff is not secured in a sufficient quantity and very often also quality, in sense of required broadness of knowledge. The target of the described activity is to overcome this obstacle.

The progress to the final target consists of several steps requiring the cooperation of a spectrum of institutions able to cover the relevant topics in required broadness. The methodology used in the present case may be described as follows:

- Identification of the outline structure of the programme proposed,
- Identification of the suitable partners having expertise in the related fields,
- Setting up the detailed study programme curriculum broken down to the individual lectures,
- Producing content for the programme developed,
- Piloting the programme proposed at the selected universities,
- Collecting feedback from the students as well as from the teachers involved in piloting,
- Producing a final version of the programme content,
- Applying for programme accreditation.

As the most relevant degree of study, a Master programme was selected for this project. This is because a Masters degree allows more substantial specialisation on hydrogen technologies based on engineering fundamentals obtained during the Bachelor degree study. A second initiative is oriented towards continuous professional development (CPD). Both these activities allow to train a significant number of specialists needed for the transition to the hydrogen economy implementation quite rapidly.

The course content elaborated is prepared in the way to be available in a repository and organised such as to allow high quality distance learning. A limitation is represented by at least 20 % of the course content to be delivered at the participating University locally in face-to-face fashion. Participation of partners from various European countries ensures translation of the materials produced to a number of languages in order to make them more attractive for the students as well as for the Universities. Project core partners will provide the necessary support towards the realisation of the study programmes and in keeping the content up to date.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 779730. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.

Boosting Aqueous Zinc Batteries by Intercalation Chemistries at High-Voltage

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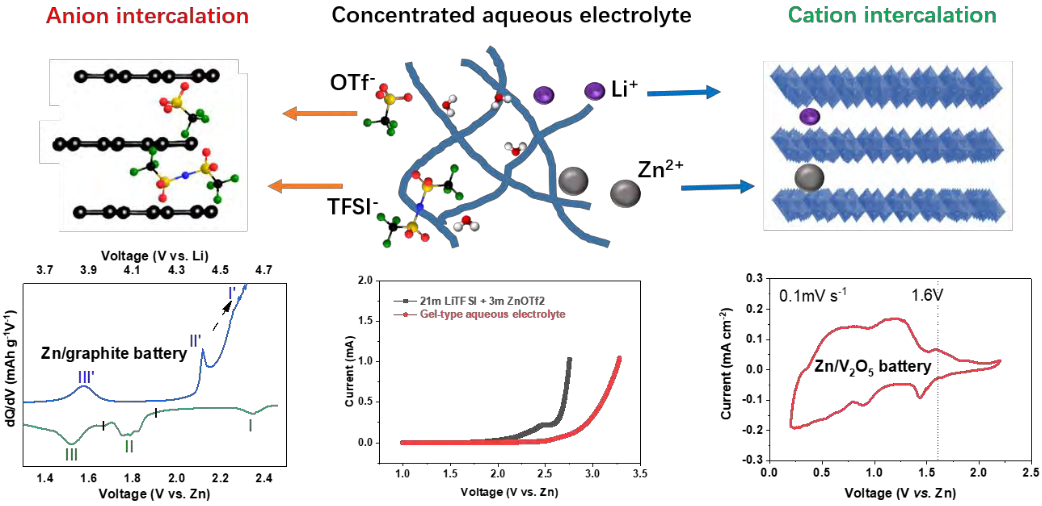
Aqueous batteries are highly desirable for large-scale energy storage. However, the energy density and cycling stability are major issues for their applications. Rechargeable aqueous zinc batteries have a direct advantage as they can employ Zn metal as negative electrode.[1] However, their development is plagued by the reversibility of Zn anode and a limited choice of positive electrodes, which often show inadequate cycling life and low energy density. Recently, the concept of highly concentrated electrolyte enables the wide electrochemical stability window of aqueous solution, providing the basis for the development of high voltage aqueous batteries.[2,3]

Here we demonstrate the intercalation reactions in optimal aqueous electrolytes for high-voltage aqueous zinc batteries. The designed aqueous concentrated electrolytes can manifest superior Zn stripping/plating reversibility, combined with a promising electrochemical stability window. Firstly, we investigated the reversible anion intercalation reaction in graphite positive electrode for aqueous zinc battery, as a concept of dual-ion battery. This cell offers a high operating voltage and unprecedented cycling stability with comparable Coulombic efficiency. Further, we report the high-voltage intercalation reaction of V_2O_5 positive electrode using a concentrated gel polymer aqueous electrolyte for zinc batteries. Quasi-solid-state Zn/V_2O_5 batteries employing such an electrolyte, reach a high operating voltage of 2.2 V, resulting in a specific energy of 326 Wh kg^{-1} at 20 mA g^{-1} based on cathode mass, and a capacity retention of 93% over 600 cycles at 500 mA g^{-1}. Moreover, the cell well performs in the 0-40 °C temperature range without significant energy loss. These results may open up the development of high-voltage aqueous Zn batteries employing intercalation-based positive electrodes leading to potentially high energy, high reversibility and high safety.



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Data-Driven Design of Microstructure in All-Solid-State Batteries

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Since the discovery of practical sulfide superionic conductors in 2016 [1], all-solid-state batteries (ASSBs) have been considered as one of the most promising candidates for next-generation batteries. ASSBs are not only high-powered but also electrochemically stable. These properties enable a wide selection of high-capacity active materials, some of which are incompatible to liquid-state batteries. In contrast, ASSBs have a difficulty in making contact interfaces between solid particles, even though this is a negligible problem for liquid-state batteries. Repeated charge / discharge cycles cause disconnects in inter-particle interfaces, resulting in shortening battery life. This degradation phenomenon is derived from a crack propagation phenomenon in a heterogeneous powder mixture, and accurate prediction is extremely difficult to deal with existing simulation methods. Solving the problem of interfacial contact and preventing degradation are one of the most important issues toward the practical application of ASSBs.

Recently, battery degradation research by data-driven approach was successful in accurately predicting battery life in various charge / discharge patterns [2]. This indicates that the data-driven approach is more effective than a simulation-based approach in predicting battery life. However, the input data in this study was acquired from mass-produced and identical batteries with extremely low variance of properties that meets the product standard. In other words, this study provides optimal control methods for suppressing degradation of the identical batteries, but does not provide a better battery design to extend its life.

Therefore, we studied a new data-driven method to explore a better electrode design. As experimental insights, ASSBs' lives differ in different manufacturing processes, even though the design values and materials composition of the samples are completely same. One of the causes is considered to depend on a microstructure inside a battery, particularly spatial distribution and relative positions of each materials [3]. Therefore, we acquired 17,700 scanning microscope (SEM) images from 177 various design of batteries in order to investigate the relationship between the microstructures and the batteries lives. In this presentation, we discuss the results of recognized degradation patterns through image generative model using two pairs of images from fresh and degraded batteries.

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Tripodal Anchoring Groups for Molecular Electronic Elements.

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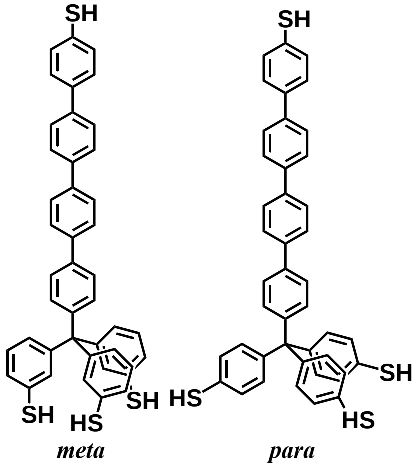

Knowledge of the conductance properties of individual molecules is indispensable for the development of future molecular electronic devices. We have studied a series of molecules based on oligophenylene molecular wires containing tripodal anchoring groups which differ in the position of thiols (*meta* versus *para*) on the aromatic rings of the tetraphenylmethane tripod (see structures below). The conductance of individual molecules was obtained by the scanning tunneling microscopy break junction method. Density functional theory combined with the non-equilibrium Green's function formalism was used to understand charge transport properties and provide most probable metal-molecule-metal junction geometries. It was shown that in the molecules studied in this work the most probable molecular junction geometry is the following: three thiolates of the tripod are anchored to one electrode and a single thiolate of the oligophenylene wire to another one. The junction formation probability for *meta* functionalization was 68 % and that for *para* 55 %, respectively. Nevertheless, the conductance-distance histograms for both molecules show two peaks, where a high conductance peak G_H represents the conductance through a tripodal platform, whereas the low conductance peak G_L represents conductance along the molecule through the tripod-linked molecular wire as described above. Single molecule conductance for *meta* functionalized wire is $\log G_H/G_0$ (meta) = –3.7 ± 0.6 and $\log G_L/G_0$ (meta) = –5.8 ± 0.5 and that for *para* functionalized wire is $\log G_H/G_0$ (para) = –3.9 ± 0.6 and $\log G_L/G_0$ (para) = –5.6 ± 0.5, respectively. These results indicate that *meta* substitution leads to a more stable junction compared to *para* molecules, whereas *para* functionalized tripodal anchoring group has better conducting properties. Experimental and theoretical results will be further discussed in terms of the suitability of these types of molecules as supporting conductors for additional molecular electronic elements important for the future molecular electronics design.[1–4]

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Electrochemical Processing for Small-Scale Robotics

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We live in a world increasingly surrounded by robots such as robotic surgical systems, flying drones, autonomous planetary rovers, and robotic appliances. An emerging family of robotic systems are untethered micro- and nanorobots. These tiny vehicles can move either by harvesting chemical fuels present in their swimming environments or by means of external energy sources. One of the ultimate goals of small-scale robotics is to develop machines that can deliver drugs, or realize other medical missions in confined spaces of the human body. Other applications include water remediation or "on-the-fly" chemistry. The recent rapid developments in small-scale robotics is undeniably related to advances in material science and manufacturing. However, while many applications have been demonstrated, aspects such as complex locomotion, multifunctionality, biocompatibility and biodegradability need to be further investigated for the successful translation of these devices to real applications. To this end, new material-based concepts and novel fabrication schemes are urgently required.

Electrochemical processing techniques have played a significant role in the development of materials for small-scale robotics. Electroless, electroforming, electrodeposition and anodization – to name a few – have been widely used as batch manufacturing approaches for the fabrication of micro- and nanorobots. In this talk, I will introduce some of our latest developments in small-scale robotics using electrochemical processing techniques. Particularly, I will show how 3D printed microtemplates can be exploited to produce complex robotic microstructures made of electrodeposited rigid metals, soft polymers and combinations of these. As a result, topologically complex metal-organic structures can be realized with sub-micrometric resolution. I will also demonstrate that metal-organic interlocked micromachines can solve several practical challenges in small-scale robotics. We will show that high magnetic responsiveness, drug loading capabilities, biocompatibility, on-demand shape transformation, and multi-locomotion modes can be embedded in a single microrobotic machine.

Mixed-Valence CoMn Layered Double Hydoxides Nanoparticles as Efficient Electrocalalysts for Hydrogen Peroxide Sensing

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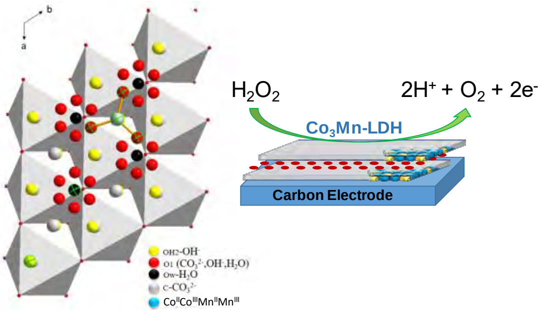
Among the nanomaterials reported in the literature for electroanalytical applications, hybrid and biohybrid materials or nanocomposites based on layered double hydroxides (LDH) have been used as electrode modifiers for sensing environmental pollutants or small biomarkers, such as glucose or hydrogen peroxide[1,2]. LDH are lamellar materials made by the stacking of positively charged brucite-like layers separated by intercalated charge-compensating anions and water molecules. They are represented by the general formula $[M^{2+}_{1-x} M^{3+}_{x}(OH)_2][X^{m-}_{x/m},nH_2O]$ with M^{2+} and M^{3+} being divalent and trivalent metal cations, respectively and X^{m-} the anionic species. Interestingly, the LDH have a unique inorganic structure that can combine mixed-valence transition metal cations (i.e. NiFe, NiCo, CoMn, CoFe, etc.) in its framework. These LDH containing transition metals are, since very recently, under great investigation, in particular for their electrocatalytic behavior for water splitting, as well for electroanalytical applications[2,3].

A series of Co_RMn-LDH ($1 \leq R \leq 5$) was synthesized by the coprecipitation method. The formation of LDH phases is confirmed by powder X-ray diffraction (XRD) and infrared spectroscopy (FTIR). The energy dispersive X-ray analysis (EDX) confirms the total coprecipitation of Co and Mn and the X-ray photoelectron spectroscopy (XPS) gives evidence of the joint presence of Co(II), Co(III), Mn(II), Mn(III) in the LDH structure. The Rietveld refinement of the structure using the XRD data reveals that the sample with a Co:Mn ratio 3:1 displays a pure LDH phase having an unusual trivalent metal composition, with a M(II):M(III) near 1:2 and a high content of CO_3^{2-}/OH^- charge compensating anions in the interlayer.

When compared with the other Co_RMn-LDH, the Co_3Mn-LDH displays the best redox properties in an alkaline medium (0.1 M NaOH) and in a neutral pH (0.1 M Tris buffer at pH 7). An in-depth study of the Co_3Mn-LDH obtained after electrochemical oxidation was performed and its electrocatalytic behaviour for H_2O_2 oxidation at neutral pH was evaluated using cyclic voltammetry and chronoamperometry. The Co_3Mn-CO_3 modified electrode exhibits good electrocatalytic performance in terms of sensitivity 30 mA M^{-1} cm^{-2} and a detection limit of 86 µM. These values can be compared to those reported for electrochemical sensors based on other LDH or mixed spinel oxides, showing the interest of bifunctional CoMn-LDH in sensing H_2O_2 in neutral pH under oxidation condition. Finally, Co_3Mn-LDH was used as immobilization matrix for glucose oxidase (GOx) to build bioelectrodes which have been tested for the electrochemical detection of glucose.



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Charge Transport Tuning in Electrolyte-Gated Field Effect Transistors by Electrochemical Approach: Inkjet-Printed Graphene Oxide Electronics and Applications

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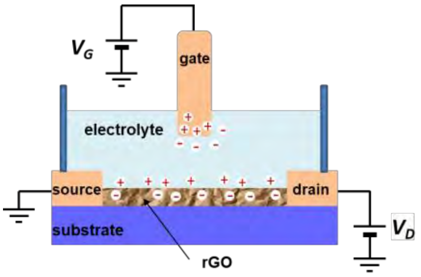

Figure 1. EG-GFET configuration scheme with inkjet-printed rGO as the active layer.

Graphene and its derivatives have been extensively studied and used for a wide range of applications thanks to their outstanding characteristics: high values of charge mobilities, high electronic sensitivity toward outside interactions and excellent conductivity.[1] Used as the active layer in electrolyte-gated graphene field-effect transistors (EG-GFET; Fig. 1), its charge carriers density can be modulated with an appropriate gate voltage.[2] In this work, the inkjet-printing technique is employed for the deposition of the graphene active layer in the GFET structure, using our own formulation of graphene oxide (GO) printable ink. This allows us to obtain an EG-GFET in a timely, effective manner and at low cost. The as-printed GO layer is then electrochemically reduced (rGO), using an *in-situ* approach that we developed on the bottom-contact configuration of GFETs[3,4]. Morphology of the printed layer as well as its electrical properties are studied (Fig. 2a). Reduction degree is observed to significantly affect the charge transport in rGO, leading both to the control of charge carriers' mobility as well as its doping level. In terms of applications, we study this EG-GFET for the life cycle monitoring of photosynthetic organisms (Fig. 2b). During the photosynthesis (under illumination of the cyanobacteria *Anabaena flos-aquae* here studied) oxygen is released in the solution and reduced at the gate, which permits its detection in terms of increase of the device output current. On the contrary, during the respiration process (occurring in the absence of light) there is a decrease of oxygen concentrations due to its consumption by cyanobacteria, resulting in a decrease of the device current. Furthermore, we study and present the effects of water pollutants on the metabolism of cyanobacteria.

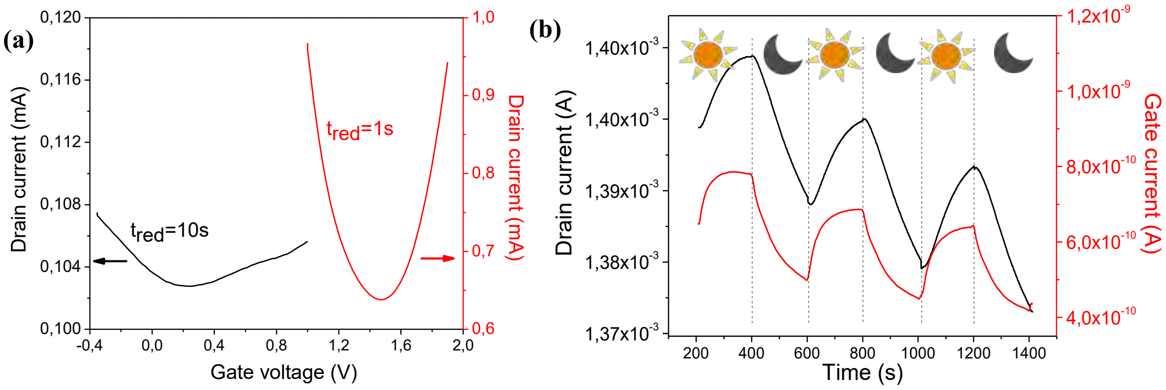

Figure 2. **(a)** Electrical characterization of rGO for different reduction times (arrows showing the corresponding current axes of each transfer curve). **(b)** Chronoamperometric study of cyanobacteria's metabolism in the presence (current increase) and absence of light (current decrease) in rGO-EG-FET configuration.

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Electron Transfer Kinetics in a Deep Eutectic Solvent.

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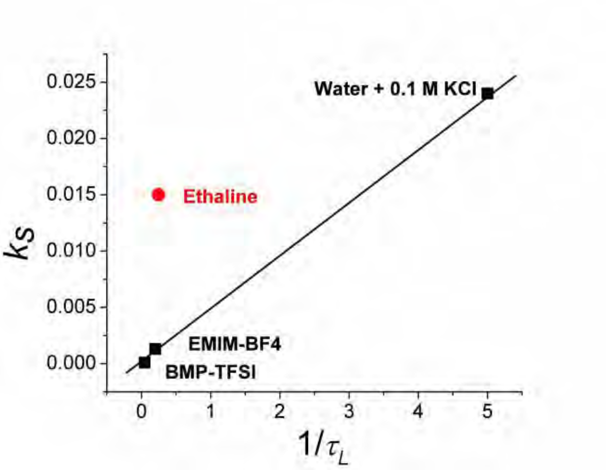
Since their initial proposition, Deep Eutectic Solvents (DES) are receiving an increasing interest as new class of solvent for numerous applications ranging from synthesis, electrochemistry to extraction, etc.[1] Common DES are often composed of a salt and a hydrogen bond donor. They are now considered as possible electrolytic media because of their inherent ionic conductivity associated to excellent solubilizing properties. Moreover, they are easy to prepare, low cost and possibly environmental friendly.

Electron transfers (ET) rate in these media is a key parameter for many proposed electrochemical applications. In this work, Electron Transfer (ET) kinetics in Ethaline that is one of the most common DES (1:2 Choline Chloride + Ethylene Glycol) have been investigated with the example of two common redox couples (ferrocene/ferrocenium and ferrocyanide/ferricyanide). Accurate analysis of a fast electron transfer in such media is a challenging task because of a lower viscosity and conductivity that required a careful treatment of the residual ohmic drop.

Rate constants are discussed in the framework of the Marcus-Hush theory and compared with values in molecular solvents or common ionic liquids.[2] They were found to be close to the values reported in organic solvent for ferrocene oxidation or in water for ferrocyanide oxidation. In that sense, Ethaline appears to be more similar to a molecular solvent than to an ionic liquid.[3,4] We could connect this observation with another observation concerning the small variations of the diffusion coefficients with the charge of the solute as observed previously in Ethaline and in Reline.[5] This behavior is in sharp contrast to the observations in ionic liquids where diffusion coefficients vary with the charge carried by the solute because of specific interactions between the molecules and the ions of the ionic liquids.
When considering DES for electrochemical applications, the fast electron transfer is a strong advantage of these media for example in energy storage systems or electrochemical sensors where the current density or time response is a key parameter.



Variations of k_s for the ferrocyanide/ferricyanide couple versus $1/\tau_L$

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Energy Conversion and Storage:
Novel Materials and Operando Methods

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This presentation will deal with the development of new materials and *operando* methods for energy conversion and storage with emphasis on fuel cells and battery materials and technologies. The presentation will begin with a brief overview of the methods employed. Particular emphasis will be placed on the use of X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) X-ray microscopy and tomography and transmission electron microscopy (TEM) under active potential control. The utility of these methods will be illustrated by selected examples including electrocatalysts for the oxygen reduction reaction (ORR), hydrogen oxidation reaction (HOR) and spectroscopic studies of Li/S and Li/Se batteries and Li metal deposition and dendritic growth. The presentation will conclude with an assessment of future directions.

Enabling multivalent batteries by organic cathodes

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Classical insertion chemistry in multivalent batteries has only limited success due to different difficulties connected with a diffusion of highly polarizable multi valent cation, with a charge transfer reaction due to strong solvation, and electrolyte components that are not compatible with high voltage cathode materials based on oxide framework. Much better and stable electrochemical activity can be obtained by use of redox active organic polymers. Although organic materials possess low volumetric energy density, in the combination with high volumetric energy density metal anodes (magnesium, calcium or aluminum), still can offer highly interesting battery system with practical application. Moreover, multivalent organic batteries are attractive due to sustainability, safety and environmental aspect connected with decreased CO_2 release. As in the case of insertion cathode materials, multivalent organic batteries have only limited choice of electrolytes, since they need to have non-nucleophilic character, excellent ability for stripping and deposition and suitable electrochemical stability.

In this presentation, overview of recent achievements in our group on the field of organic multivalent batteries will be discussed with a focus on the proper selection of battery components in order to achieve electrochemical properties attractive for the commercialization.

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Water-in-salt electrolyte: from hype to practical reality in Li-ion battery

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Sustainability of battery components is becoming nowadays an overriding parameter for storing renewable energy at large scale. Towards that ambitious goal, several strategies are currently being explored. One of them is the use of aqueous electrolytes that are theoretically cheaper, safer and less toxic than their organic counterparts. However, the major limitation towards the development of aqueous electrolytes is the narrow thermodynamic electrochemical stability window (ESW) of water (1.23V). Although, it can be kinetically extended to 1.5V when using salts in diluted solution, it remains not competitive when compared to organic solvent. Owing to this limitation that translates into poor energy density, Li-ion aqueous systems, as introduced in 1994 by Dahn, and coworkers could never be marketed [1].

To alleviate this issue, Suo *et al.* [2] proposed in 2015 an aqueous electrolyte made with a high salt concentration (21mol/kg), denoted *Water-in-salt* (WiSE), which they claim to enlarge the operating potential window to 3V and possesses a conductivity close to that of classical organic electrolyte (ar. 10mS/cm). Following this initial discovery, Yamada *et al.*[3] then showed that *Water-in-bisalt* enables to build batteries with a potential up to 3.1V. Both studies have renewed interest for studying aqueous systems. Nevertheless, a few question dealing with practicality of such findings remained. Herein, we carried out a systematic study to assess the practical viability of 20mol/kg LiTFSI *Water-in-salt* electrolyte. To do so, two couple of electrodes were chosen to decouple the influence of *WiSE* on cell performances : Mo_6S_8/*WiSE*/LFP was chosen on the cathodic side and $LiTi_2(PO_4)_3$/*WiSE*/NMC_{622} on the anodic side to study how the competing water reduction (HER) and oxidation (OER) affects the system performance. Electrochemical tests were performed to estimate cell performances as a function of concentration, temperature and cycling rate. The influence of parasitic reactions on battery performances was studied by online electrochemical mass spectrometry (OEMS), while cyclic voltammetry and self-discharge experiments enabled the assessment of SEI stability.

Thus, we found that water reactivity it not suppressed by the used of WiSEs with continuous generation of gas upon charge. Indeed, continuous SEI dissolution is monitored, which leads to drastic self-discharge and poor efficiency at low C-rate. This systematic study therefore leads us to conclude that *Water-in-salt* electrolyte cannot be used for practical application in Li-ion battery.

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Water-Gated Organic Field Effect Transistor for Monitoring of Photosynthetic Organisms

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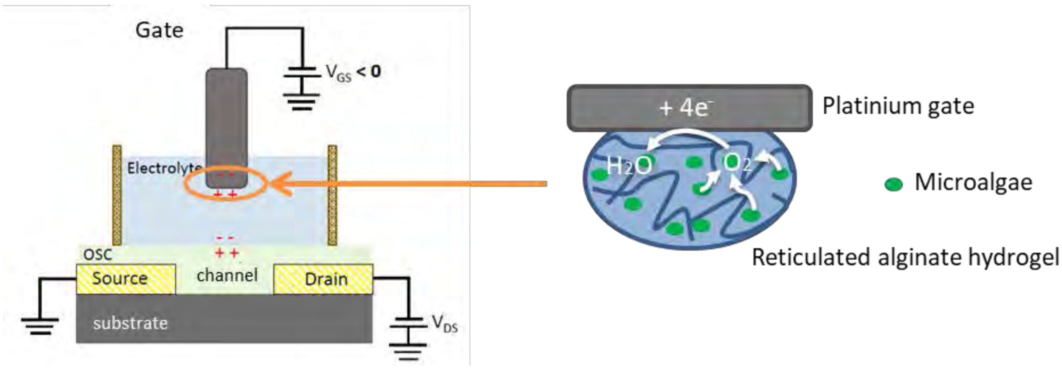
Organic Electrochemical Transistors (OECTs) are frequently reported for cell monitoring[1]. In contrast, Electrolyte Gated Organic Field Effect Transistors (EGOFETs) have never been described for that kind of application. However, water-gated OFETs seem perfectly adapted for this because they can operate directly in a cellular culture medium, thanks to the conventional dielectric layer being replaced here by water[2]. They are possibly more sensitive than OECTs due to their much higher *on/off* ratio (several thousands instead of several tens).

In this work, we first demonstrate that not only the gate potential can trigger the source-drain current, which is the generally accepted mode of operation, but that the current flowing at the gate can also be used, providing that the gate/electrolyte capacitance stays significantly lower than that of the electrolyte/semiconductor interface.

As an example of application of this new mode of operation, we aim to demonstrate here that monitoring microalgae photosynthesis is possible through the direct measurement of photosynthetic O_2 production thanks to its electroreduction on the EGOFET's gate. Microalgae (*Anabaena flos aquae*) are tapped within an alginate hydrogel[3,4] grafted on the platinum gate. While doing photosynthesis, microalgae produce O_2 that is electroreduced on the gate; the resulting current significantly decreases the gate/electrolyte potential drop and symmetrically increases that of the electrolyte/semiconductor interface, leading to an increase of drain current.



EGOFET structure under negative polarization and strategy of gate modification

Beyond this proof of concept, a possible application is the environmental monitoring of pollutants cocktails through their deleterious influence on the metabolism of photosynthetic organisms such as microalgae or cyanobacteria. This also paves the way for novel applications of EGOFETs in the field of amplification of redox reactions in general.

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Biotic/Abiotic Photo-Bioelectrochemical Cells for the Generation of Electrical Power

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The photosynthesis process converts light energy into useful fuels (hydrocarbons) by coupling light and dark cycles. This Fundamental process enables the earth's energy demands in the last 3.5 billion years. The light cycle coined “Z-scheme”, facilitate efficient light-induced charge separation processes, which lead to the generation of chemical fuels. While photosystem II coupled to electrodes can oxidize water to evolve oxygen and generate photocurrent, photosystem I can be utilized in both directions to generated anodic or cathodic photocurrents. The direction can be controlled by an applied bias, utilization of redox mediators or the use of electron donor (or electron acceptor). In the last few decades, numerous attempts to mimic the photosynthetic process have been realized using different scientific approaches drawn from different disciplines, but the quest for a sustainable world is still in its course.

Here we present the development of biotic/abiotic based photoelectrochemical cells, which facilitate photoinduced electrical power generation. The developed cathodes which are based on Photosystem I or Bilirubin Oxidase facilitate efficient oxygen reduction reactions. By coupling those developed cathodes to BiVO4 based photoanodes, bias-free, donor free photo(bio)electrochemical cells that generate electrical power can be obtained.

Two major configurations will be discussed and presented:

a. A donor-free photobioelectrochemical cells for the generation of light-triggered electrical will be presented. The developed oxygen reduction biocathodes are based on bilirubin oxidase (BOD) originates from *Myrothecium verrucaria* (MvBOD) and a thermophilic *Bacillus pumilus* (BpBOD). Methods to entrap the bilirubin oxidase with ABTS redox molecules in a polydopamine layer will be presented and a pH-independent, positively charged pyrene-betaine linker Both developed polydopamine/ABTS/MvBOD and the pyrene-betaine/BpBOD biocathodes were further coupled with BiVO4/cobalt-phosphate water oxidation photoanodes to construct biotic/abiotic photobioelectrochemical cells, generating power outputs of 0.74mW/cm^2 and 0.85 mW/cm^2, respectively.

b. We further show the development of a layer-by-layer photocathode configuration, which utilizes a thermophilic photosystem I for the generation of electrical power. Two redox-active polymers were used, polymethylene blue (pMB) which acts as an electron donor and poly-butyl-viologen, (PBV) which acts as an electron acceptor and as a catalyst for oxygen reduction. The redox-active polymers enable improved stability, improved PSI trimers integration on the electrodes and facilitates efficient charge separation processes. The developed photocathodes were further coupled to BiVO4 for the construction of donor free, bias-free photo(bio)electrochemical cells.

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Bottom-up electrosynthesis of BiTePd nanofilm using electrochemical atomic layer deposition technique for ethanol oxidation

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Abstract

Nanofilms have increased a considerable interest in fuel cell due to their high electrocatalytic performance. Electrochemical atomic layer deposition (E-ALD) is low temperature and a low-cost electrodeposition technique which sequentially produces nanofilm materials [1]. In this work, E-ALD cycles were used to electro-synthesize rarely BiTePd nanofilm on Au substrate via alternated surface limited replacement (SLRR) of copper underpotential deposition (Cu-_{UPD}) and repetitive execution of oxidative Te-_{UPD} and reductive Bi-_{UPD}. In order to set optimal potentials for E-ALD cycles, the electrochemistry profile of Au and Pd surface in Te^{4+} and Bi^{3+} solutions was investigated using cyclic voltammetry (CV). It appeared that the atomic layers of Bi, Te may form via UPD and overpotential deposition (OPD) respectively. The resulted deposits consist of unitary (Te, Pd), binary (BiPd, TePd) and ternary (BiTePd) nanofilms. All the deposits exhibit the typical Pd signatures, with the varied current response and potential shift of Pd-O oxide around -0.2 to -0.16 V vs. Ag/AgCl. The detailed studies of structure-composition were obtained using XRD, SEM-EDS, and AFM. TePd and BiTePd exhibit nanodendritic structure with alloy and elemental phases textured epitaxial along Pd-Au (111) orientation. EDX evidenced the presence of all deposited elements. Moreover, ternary and binary nanofilms showed higher electrocatalytic activity and stability towards EOR than unitary Pd confirmed by the following trend (peak current and onset potential): BiTePd (1.26 mA, -0.55 V)> TePd (0.527 mA, -0.535V)> BiPd (0.24 mA, -0.39 V)> Pd (0.135 mA, -0.35 V) obtained from CV and Chronoamperometry (CA). The incorporation of Bi and Te on Pd surface improved interfacial charge transfer during EOR using electrochemical impedance spectroscopy (EIS). These results encourage the use of ternary BiTePd nanofilm electrocatalyst for application in alkaline direct ethanol fuel cells (DEFCs).

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Sustainable Electrochemical Metal Extraction from Waste Streams: From Removal to Recovery

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Abstract: Due to the wide spread development of chemical, electronic, metallurgy and energy, considerable hazardous heavy metals-bearing wastewater and solid waste are directly or indirectly discharged into the environmental. In order to overcome the drawbacks of long process-flow and large chemicals requirements in conventional treatment technologies, novel electrochemical metal extraction techniques are developed in this study including alkaline electrochemical oxidation processes (A-EAOPs) and cyclone electrowinning (emew® cell). Efficient and selective metal extraction is achieved from refractory spent SCR catalysts and vanadium slag via in-situ generated reactive oxygen species (ROS), while controllable Cu, Te, Se powdery products are obtained from dilute multi-component wastewater. Besides, the electrochemical recovery mechanism and behavior are revealed using in-situ dynamic X-ray synchrotron imaging and fluid flow calculation techniques, particularly in the complicated HCl effluents. Based upon the systematic investigations of reactors, mass transfer, phase transition and electrochemical reactions, the process-mechanism-products (PMP) rational design of electrochemical metal recovery is proposed rather than simply metal removal.

Keywords: Metal recovery, Reactive oxygen species, Mass transfer, in-situ dynamic X-ray imaging, Process-mechanism-products (PMP)

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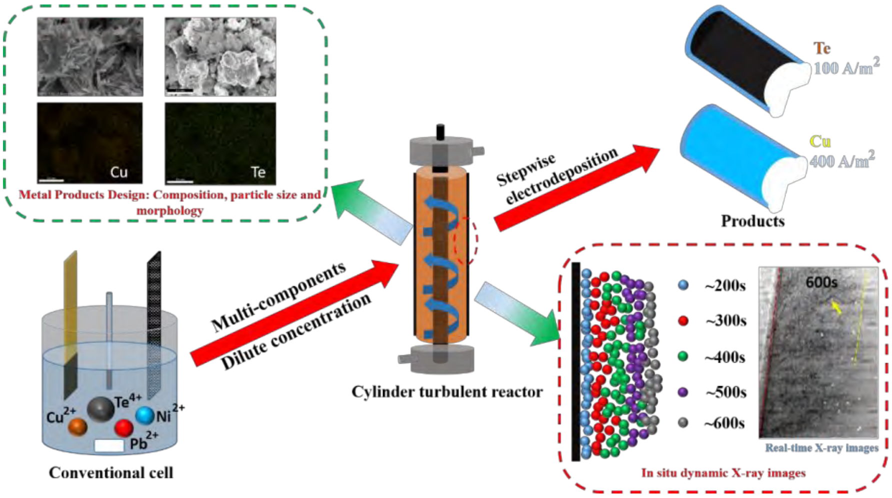

Fig. 1: The process-mechanism-products (PMP) during electrochemical metal recovery

Phase diagrams under scrutiny – In-situ electrochemical X-ray diffraction unravels layered β-Fe_{1+x}Se as superconductor for all x

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Systematic investigations of phase systems and transitions are the foundation of understanding complex physical phenomena such as superconductivity. One example in which the lack of such a systematic knowledge has led to contradictory results is β-Fe_{1+x}Se. The superconductivity of this “simple” two-dimensional, layered structure has been reported to be heavily dependent on the composition and closely related structural transitions, defects and various superstructures with overall very inconsistent results.[1–6]
The difficulties arise from the narrow phase width of β-Fe_{1+x}Se ($0.01 < x < 0.04$), a small deviation from the 1:1 ratio and its manifold of neighbouring phases.[7]
We report the precise post-synthetic control of the composition of β-Fe_{1+x}Se by electrochemistry with simultaneous tracking of the associated structural changes via in-situ synchrotron X-ray diffraction (Figure 1).[8] Via an externally applied potential, electrochemistry allows us to systematically explore the phase system, while affording the high precision needed in this case. We confirm the phase width of $0.01 < x < 0.04$ and identify the superconducting state below 8 K, which in contrast to earlier reports is independent of the composition. However, in a second set of in situ X-ray diffraction experiments, we demonstrate that β-Fe_{1+x}Se forms a new phase in the presence of oxygen above a 100 °C, which has the same anti-PbO type structure but is not superconducting down to 1.8 K. The latter process can be reversed electrochemically to reinstate the superconducting state.
This electrochemical approach takes experiments for two-dimensional materials beyond intercalation reactions,[9,10] and exploits the exquisite control provided by electrochemistry.

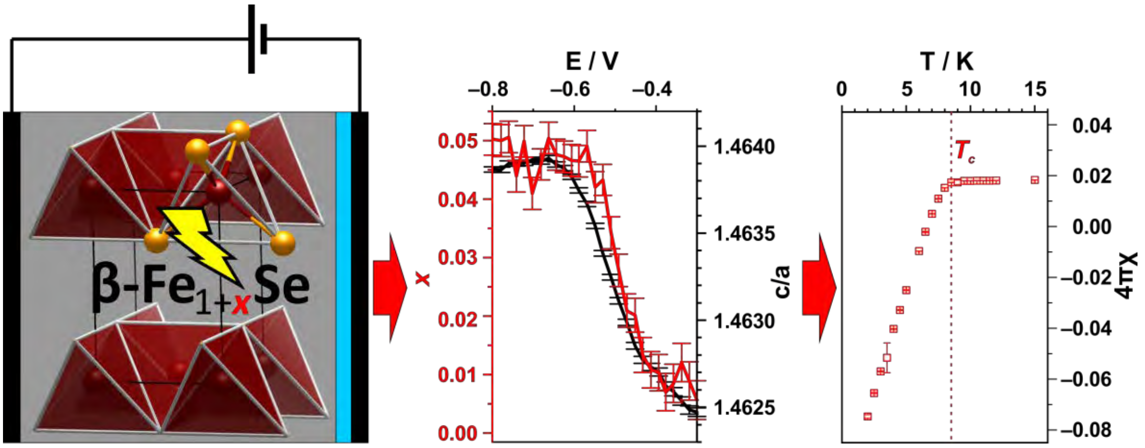

Figure 1: The composition of β-Fe_{1+x}Se (left) is electrochemically varied within its phase width (center: red). Simultaneously, the structural changes are monitored via X-ray diffraction (center: black). Independent of the composition, the superconducting transition temperature remains unchanged (right).

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PQQ-Glucose Dehydrogenase-Calmodulin Chimera Enzyme: Different Triggered Activation for Multipurpose Biosensors

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In the last decade, the rise of synthetic biology has driven the efforts to construct artificial allosteric protein switches in order to detected and quantify natural and artificial chemistries in vitro and in vivo. Typically, this involves construction of chimeric enzymes via insertion of a regulatory receptor domain into the biocatalytic reporter domain. Construction of such chimeric enzymes utilizes the recombinant DNA technology that is a core technology of protein engineering [1].

Herein, we report on the bioelectrocatalytic properties of pyrroloquinoline quinone-dependent glucose dehydrogenase fusion with calmodulin (PQQ-GDH-CaM). This protein is catalytically inactive in its ground form but can be activated by the addition of calmodulin binding peptide that induces its conformational transition and activation, as shown in Figure 1. The PQQ-GDH-CaM was immobilized onto highly porous gold (hPG) produced electrochemically [2] by using a bifunctional linker, namely 4-mercaptobenzoic acid further activated through 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide and N-hydroxysuccinimide (EDC/NHS) coupling to covalent bind the PQQ-GDH-CaM chimeric enzyme [3].

At first, we characterized the switchable features of PQQ-GDH-CaM by simply exposing it to the activating peptide. Subsequently we devised an approach to use proteolytic activation of a caged-peptide to generate activating peptide for PQQ-GDH-CaM. Furthermore, the system was utilized to study different pathways for PQQ-GDH-CaM triggered activation according to different logic gates in order to realize multipurpose biosensors (e.g., glucose detection, peptide detection etc.) [4].

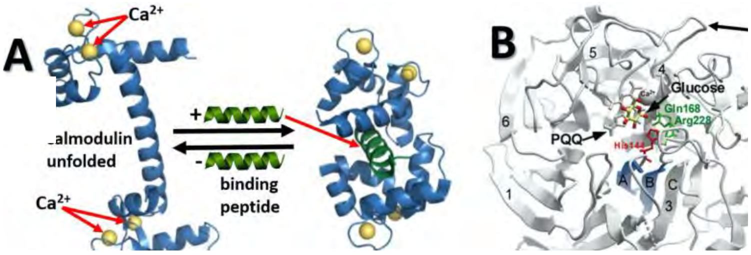

Figure 1. Activation mechanism of PQQ-GDH-CaM by the addition of calmodulin binding peptide

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How Ionophore-Valinomycin Enters and Transports K$^+$ Across a Model Bilayer Lipid Membrane

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Valinomycin, a cyclic peptide, was incorporated into a biomimetic lipid membranes either tethered (tBLM) to or floating at the surface of a gold (111) electrode. Electrochemical Impedance Spectroscopy (EIS) was used to study the ionophore properties of the peptide and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) was employed to determine the conformation and orientation of valinomycin in the membrane. The combination of these two techniques provided unique information about the ionophore mechanism where valinomycin transports ions across the membrane by creating a complex with potassium ions and forming an ion pair with a counter anion. The ion pair resides within the hydrophobic fragment of the membrane and adopts a small angle of ~22° with respect to the surface normal. This study provides new insights explaining the valinomycin ion transport mechanism in model biological membranes.

Su, ZhangFei; Ran, Xueqin; Leitch, J. Jay; Schwan, Adrian; Faragher, Robert; Lipkowski, Jacek, "How ionophore-valinomycin enters and transports K+ across a model bilayer lipid membrane", Langmuir, **2019**, 35, 16935-16943

Nano-Crystalline Graphene Electrodes for Anthracene Sensing

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The nano-crystalline graphene (NCG) shares electrical characteristics matching few-layered graphene in terms of sheet resistance, meanwhile the electrochemical features, reflected by the heterogeneous electron transfer rate constant, are closer to the highly oriented pyrolytic graphite (HOPG - basal plane). Therefore enhancement of redox transfer at NCG electrodes is promoted through an increase of the availability of edges, obtained under a pre-activation step, thus obtaining redox features comparable with the glassy carbon electrode (GC). The advantages related to the use NCG as electrode material are ascribed to its reproducible PECVD synthesis achievable on large surfaces (wafers of several inches), its peculiar characteristics being suitable to compete with robust electrodes made of carbon fabric.

Polyaromatic hydrocarbons (PAHs) are a class of organic compounds made of hydrogen and carbon atoms accommodated in two or more fused aromatic rings, the most common known PAHs being naphthalene, fluoranthene, pyrene, phenanthrene and anthracene. Their occurrence in oils, coals, tar deposits and persistence as by-products of fuel burning made PAHs one of the most important groups of pollutants, being identified to be teratogenic, carcinogenic, and mutagenic [1]. For such a reason, anthracene is one of the 16 PAHs which are monitored routinely for regulatory purposes [2].

Graphene based nanomaterials are expected to possess properties that make them very efficient tools for the development of electrochemical sensors due to the excellent mobility of electrons in honeycomb sp2-hybridized carbons, being well known that electro-catalysis readily occurs on graphene [3].

Plasma-enhanced chemical vapour deposition (PECVD) allowed growth of graphene and N-doped graphene domains on SiO_2, consisting of densely packed nano-sized islands[4]. The Raman spectrum of the nano-crystalline graphite film, made of graphene domains, showed peaks at 1357 cm^{-1} (D band), 1600 cm^{-1} (G-band), 2695 cm^{-1} (2 D band) and 2944 cm^{-1} (D + D' bands), suggesting crystalline arrangement of graphene domains, and a certain degree of disorder.

Preliminary electrochemical investigations of NCG and N-doped NCG electrodes revealed the ability to sense anthracene and behave similar to GC electrode in terms of linear working range and applied working potential.

Acknowledgments. The authors acknowledge financial support offered by PN-III-P1-1.2-PCCDI2017-0619-"Materiale nanostructurate pe baza de carbon pentru dezvoltarea de senzori pentru monitorizarea unor gaze si hidrocarburi aromatice policiclice" - Project no. 3.

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Segmented Battery Cells for Monitoring Current Density Distribution and locally-resolved Impedance Spectroscopy Analysis

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Motivation:

As a broad market penetration of lithium-ion-batteries becomes reality in a multitude of applications, safety and reliability are major issues that have to be ensured. In recent years, especially driven by the demands and rapid growth in the field of electro-mobility, the trend in the development of Li-ion batteries goes towards the manufacturing of large-format cells to increase system energy density. In such large-format cells, thermal gradients and an inhomogeneous state-of-charge (SOC) and current distribution over the cell-stack become more significant. This can present a severe challenge regarding cycle stability and safety, which can lead to a more pronounced aging behavior as function of location in the electrode stack. In turn, it can induce performance losses, compromise lifetime and constitutes a safety issue as local hot-spots can develop at positions with higher impedance or local current density, encompassing an increase in temperature and the risk of triggering thermal degradation.

Obtaining information on how material properties, cell engineering and charge/discharge parameters influence such gradients is critical to maintain inside a safe operating window, to optimize performance and to facilitate longer lifetime.

Methodology:

To gain better insight in the above phenomena, a combination of modelling and experimental investigation, complemented by post-mortem analysis of aged cells is mandatory [1]. At the core of this work is the development of a segmented current collector which is coated by the active material and inserted into the pouch-cell as part of the electrode stack. This proprietary development [2] facilitates the real-time monitoring of local current density as function of operating conditions and facilitates performing local impedance spectroscopy on each segment distributed over the electrode. An exemplary image of this is presented in figure 1. The so-obtained knowledge is of considerable value for scientists, cell manufacturers and users, as it allows insights into locally resolved aging and the development of critical positions on the electrode surface. The experimental results further serve as validation for impedance-based cell modelling for which locally-resolved impedance data serves as input for simulation of the dynamic behavior of the cell, current density, SOC and SOH distribution during operation. This contribution will present how this combination can help in understanding the inhomogeneities in the cell and how they affect operation, longevity and performance loss of the cell.

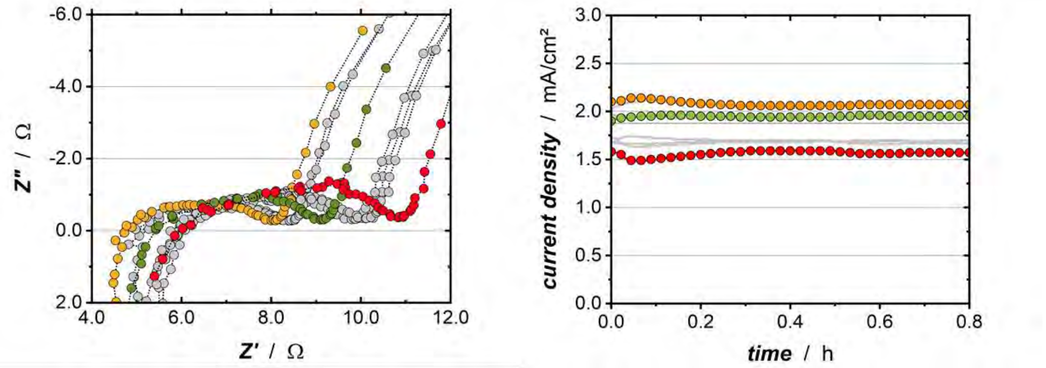

Figure 1. Proof-of-concept of segmented cell technology. Impedance spectra (left) and resulting current density distribution (right) during cycling on eight segments of the current collector.

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Multi-Physics Modeling and Empirical Investigation of Active Polymer Binder for Thick Cathode of Li-Ion Battery

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Li-ion batteries hold great importance in the process of transitioning to renewable energy. Advancement of battery technology to provide higher energy density and higher rate capability is thought to be necessary to achieve this transition. The objective of the current research work is to investigate of the effects of ionomer-based active polymer binder, in lieu of traditional binder, in the porous cathode of the Li-ion battery.

Li^+ transport within porous electrodes is limited by porosity and tortuosity. The lower effective diffusivity of Li^+, compared with the counter-anion, causes high concentration and potential gradients across the thickness of the cathode, especially at high charge-discharge rates. The depletion of the Li^+ cation from the reaction surface of active material limits the thickness of the active material that is effectively utilized at a given rates, and thus limits practical rates. Here, covalently tethered anionic ligands titrated with Li^+ are investigated to mitigate this Li^+ depletion. Ion transport properties (transference number, diffusivity, conductivity) have been characterized and used in the simulation of the multiphysics system.

For making active polymer binder functionalized nanoparticles and Poly(STFSI) were mixed with the cathode slurry. Experimental charge-discharge cycling result of the modified composite electrode (active polymer binder based) at different C-rate and thickness has been investigated and compared with the control electrode of similar thickness and porosity. The effect of active polymer on increased capacity of modified cathode is evident, after comparison.

A predictive microscale multiphysics model of the investigated system has been put in place. The governing PDEs, constitutive laws and the interface conditions (Butler-Volmer and Donnan equilibrium) that describe the electro-chemo-mechanical system have been solved numerically. A purposely written Matlab Package script has been developed and Matlab PCT has been used for parallel computing, to implement the numerical method. The discharge voltage profile and distribution of ion concentration and electric potential across the battery have been simulated. Comparison of discharge voltage profiles between the mathematical model and experimental results validate the mathematical model.

The Kinetics Study of Hydrogen Peroxide Electroreduction onto Graphene/Palladium Modified Glassy Carbon Electrode

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In present work, we report the synthesis of graphene (G) which is subsequently decorated with palladium (Pd) nanoparticles as a efficient electrocatalyst for electrochemical reduction of hydrogen peroxide (H_2O_2). The structure of obtained nanohybrid material (G-Pd) was examined by XRD technique. The graphene/palladium composite material was immobilized on the surface of a glassy carbon electrode (GCE) for the electroreduction of hydrogen peroxide (H_2O_2).

The electroreduction of H_2O_2 was studied by cyclic voltammetry (CV) and square wave voltammetry (SWV), at a potential range of −0.6 to +0.2 V in order to study electrocatalytic behaviour of G-Pd. Voltammetric data are analyzed in the light of the theory for simple irreversible electrode reaction.

The presence of palladium nanoparticles as well as Fe retained during graphene synthesis have a major role in the electroreduction of H_2O_2. The graphene/palladium composite showed pronounced electrocatalytic activity toward the reduction of H_2O_2 in alkaline medium.

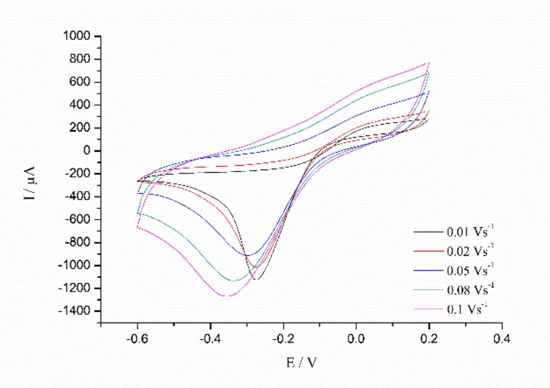

Figure 1. The CV responses of G-Pd GCE in 5 mM H_2O_2, 0.1 M KOH at scan rates 0.01, 0.02, 0.05, 0.08 and 0.1 V s^{-1}

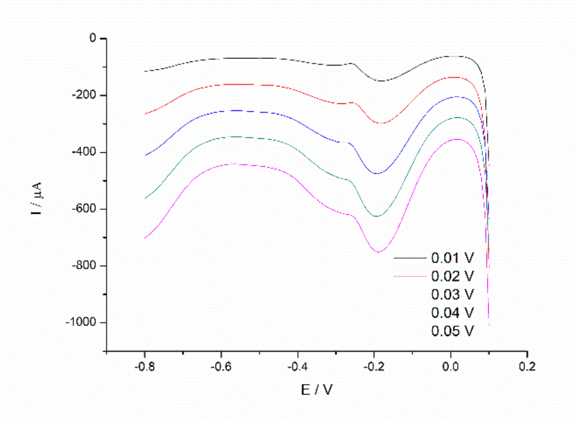

Figure 2. The SW responses of G-Pd GCE in 5 mM H_2O_2, 0.1 M KOH at amplitude values 0.01 V, 0.02 V, 0.03 V, 0.04 V and 0.05 V

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Carbon - free Ceramic Gas-Diffusion Electrodes for Secondary Zn-air Batteries

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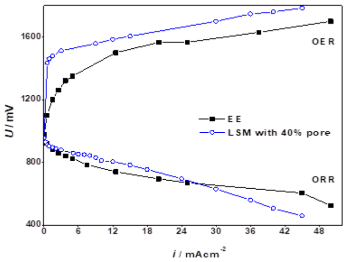
Abstract:

In recent years, secondary Zinc-air cells have received considerable attention as promising approach for energy storage of renewable energy. One of their durability problems is the oxidation of the conventional carbon gas-diffusion electrodes [1]. Replacement of the carbon-based material with ceramic one is a possible solution for overcoming this problem which is the aim of this work. An innovative approach which applies solid state "monolithic" gas-diffusion electrode proposed by standard ceramic technology is proposed. The appeared ceramic materials with perovskite structure (LSM and LSCF) provide good mechanical and chemical stability [2-4]. The solid state "monolithic" electrode is produced with 40% porosity which guarantees the necessary gas permeability. A special impregnation procedure ensures the needed hydrophobicity [5].

The testing of the new electrodes in a 1cm^2 half-cell configuration with reference hydrogen electrode. The cell was carried out subjected to cycling at charge/discharge current ± 10 mA/cm^2. The results from the electrochemical tests demonstrate behavior similar to that of the carbon-based etalon GDE. The samples are stable for more than 1000 cycles. These preliminary results demonstrate the applicability of carbon free solid state "monolithic" gas-diffusion electrodes in Zinc-air rechargeable batteries.



Comparison of volt-ampere characteristics during discharge (ORR) and charge (OER) measured on classical GDE (EE) and monolithic monolithic GDEs (LSM)

Acknowledgements:
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Non-mercury-based Electrochemical Reference Electrodes

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As an indispensable electrode in electrochemistry, the reference electrode plays a very important role in the basic research and application, which forms an electronic circuit with working electrode to achieve potential measurement and control. Currently, the reference electrodes used for electrochemical measurement in aqueous solution are generally Hg/Hg_2Cl_2, Hg/Hg_2SO_4 and Hg/HgO electrodes. The mercury-based reference electrode has the advantages of stable potential and good reproducibility. However, the electrode material contains mercury, which inevitably produces mercury pollution during the preparation, use, and recycling processes, to harm the environment and human health. In addition, mercury-based reference electrode also has the disadvantages of large temperature coefficient, severe temperature hysteresis, and inability to use at high temperature. Here we introduce Ag/Ag_2SO_4 and Ag/Ag_2O reference electrodes, to be expected to replace Hg/Hg_2SO_4 and Hg/HgO ones, with excellent potential stability, reproducibility, and lower temperature coefficient as well.

Towards Practical Li-S Battery with Dense and Flexible Electrode Containing Lean Electrolyte

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Lithium-Sulfur (Li-S) batteries attracted intensive attention as potential candidates owing to its high theoretical energy density (2600 Wh kg^{-1}) and huge natural sulfur resources.[1] The electrochemical behavior of Li-S batteries has been improved through many comprehensive strategies in recent years. Nonetheless, more realistic conditions need careful consideration towards practical Li-S battery, such as areal capacity, flexibility, electrode density, cathode porosity and electrolyte amount. The improvements favor to design real high-energy density Li-S batteries. Higher cathode loading is feasible to increase areal capacity whereas many new issues arise compared with thin-film electrodes, such as fragile cathode structure, increased electrode thickness and decreased ionic/electronic conductivity. Pressure treatment could effectively decrease electrode thickness corresponding to high electrode density and low porosity. Additionally, flexible electrode design potentially extends the application towards flexible energy storage devices.

Recently, S@pPAN has received extensive attention due to its excellent electrochemical performance. Compared with solid-liquid dissolving-deposition mechanism of common S@C composite, S@pPAN reveals unique solid-solid conversion mechanism, which enables high sulfur utilization even at low electrode porosity and lean electrolyte uptake.[2] Herein, we creatively designed a rigid-flexible coupling binder via interaction between guar gum and a novel long-chain binder carboxylic styrene butadiene rubber.[3] With sulfurized pyrolyzed poly(acrylonitrile) (S@pPAN) composite cathode, high areal-capacity cathode was fabricated with enhanced areal capacity of 5.55 mAh cm^{-2} after long cycles. Moreover, the electrode exhibited benign flexibility with a capacity retention near 90% even after 400 times' folding. In addition, remarkable electrode density up to 1.54 g cm^{-3} corresponding to cathode porosity of 13.3% and low electrolyte amount to 1.00 ml $g^{-1}_{composite}$ were proven feasible for a practical Li-S battery.

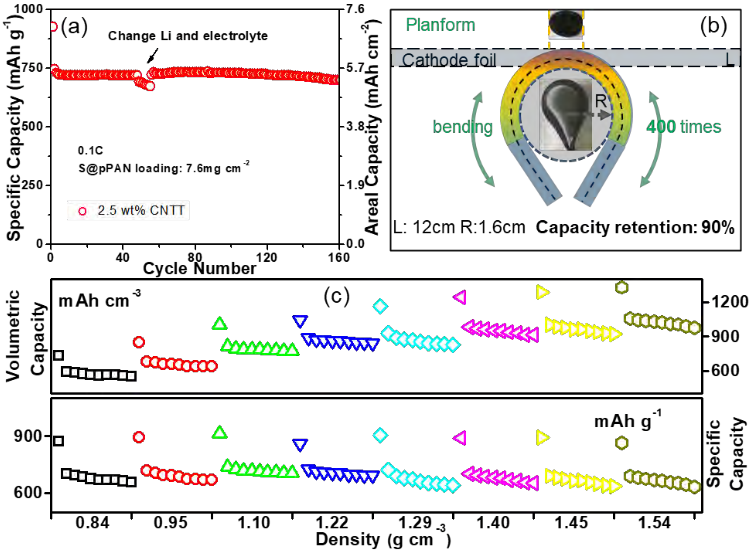

Figure.1 (a) Cycle performance of flexible cathodes; (b) Schematic illustration of bending test; (c) Electrochemical performance of flexible cathodes in different density;

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High molecular weight polyacrylonitrile precursor for S@pPAN cathode materials for rechargeable lithium batteries

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The Lithium-Sulfur (Li-S) battery has been considered as the most promising next generation energy storage system because of advantages such as high theoretical specific capacities, abundant sulfur resources, low cost and environmentally friendly[1]. For a typical Li-S battery with elemental sulfur cathode which we call as mobile sulfur, there are a number of shortcomings, such as polysulfide dissolves in the electrolyte and renders the "shuttle" effect, which leads to the loss of active materials, poor electrochemical performances, low sulfur utilization and low Coulombic efficiency. However, there is another sulfur cathode, we call it stationary sulfur, sulfurized pyrolyzed poly(acrylonitrile) (S@pPAN) which was firstly synthesized via heating the mixture of sulfur and PAN under inert atmosphere[2, 3]. The S@pPAN delivered excellent compatibility with carbonate electrolyte, high utilization of active material, and long cycle life. It is due to the fact that the material does not dissolve and has no shuttle effect of polysulfide during cycling.

Herein, we adjusted PAN precursor with high molecular weight to prepare S@pPAN with high sulfur content. For the PAN with high molecular weight, the longer main chain can form a larger conductive network and offer additional space to accommodate more sulfur molecular in the process of heating cyclization. The cathode S@pPAN, which was prepared by high molecular weight PAN precursor up to 555000 (555k), accommodated amorphous S ca. 55 wt%. It delivered reversible specific capacity of 901 mAh g^{-1} which was calculated based on whole composite at 0.1 C under 50°C with sulfur utilization over 98%, along with stable cycling and good high rate capability. Therefore, synthesizing PAN with high molecular weight as precursor is a promising strategy to effectively enhance the amorphous sulfur content in S@pPAN, which will lead to high specific capacity, stable cycling, and finally high energy density for Li-S full batteries.

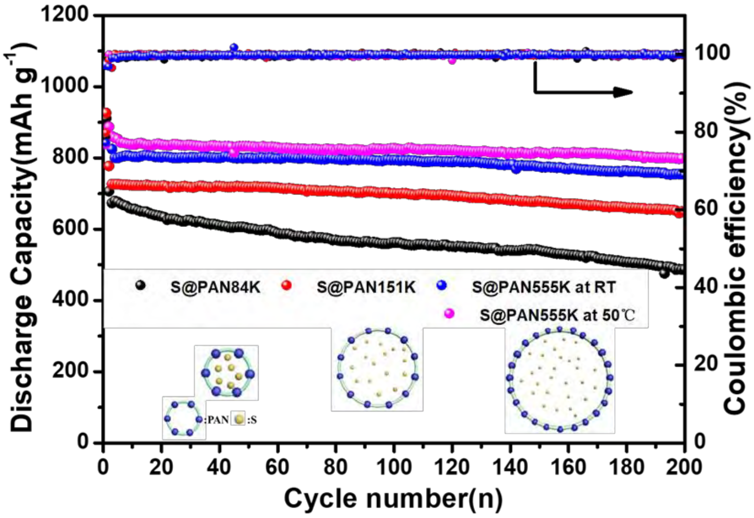

Figure.1 Cycling performance at 0.2C and Schematic of S@pPAN synthesized by PAN precursors with different molecular weights(where the number following PAN indicates its molecular weight)

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Enhanced cell performance by optimal water-uptake and electrode thickness in direct hydrazine fuel cells

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Fuel cell electric vehicles (FCEVs) have received substantial attention for its high energy efficiency and zero emission as a future alternative vehicle type to replace the conventional combustion engine-based vehicles. Direct hydrazine fuel cells (DHFCs) are the promising fuel cell type applied in FCEVs because the carbon-free hydrazine fuel does not produce any carbon dioxide and air pollutant, and its theoretical cell potential (1.56 V), energy density (5.4 kWh L^{-1}), and energy efficiency are higher than that of hydrogen gas in fuel cell system [1-2]. Further, the high catalytic activity of Ni, as an anode catalyst, toward hydrazine than precious metal Pt makes DHFCs more attractive power sources in FCEVs. Despite these strong merits, the optimal membrane-electrode assemblies (MEAs) in DHFCs operating alkaline media have not been established well, which leads to insufficient cell performance. In this research, to pursue high cell performance of DHFCs, we prepared the less oxidized Ni/C catalysts depending on the Ni contents on the carbon supports, and used the Ni/C with moderate metal contents observed for hydrazine oxidation reaction in DHFCs. We examined the effect on DHFCs performance resulting from the water-uptake in cathode and the electrode thickness in anode based on the cell evaluation. The MEAs with the appropriate hydrophobic gas diffusion layer of cathode and catalyst loading of anode showed the enhanced cell power density of 547.8 mW cm^{-2} employing the Ni/C and ultra-low amounts Pt in DHFCs [3].

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Bismuth electrodeposition in choline chloride-urea deep eutectic solvent

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Effect of ammonium chloride on bismuth electrodeposition from choline chloride-urea deep eutectic solvent (DES) using $BiCl_3$ as source of Bi(III) was investigated. Spectroscopic and thermal studies were performed on the DES in order to understand whether the addition of ammonium chloride affects its behavior; the results of the thermal study do not indicate any significant change except a modification of a cold crystallization peaks at low scan rate. The effect of temperature and NH_4Cl content on electrochemical behavior of bismuth was studied by cyclic voltammetry. Chronoamperometry was used to study bismuth electrocrystallization which indicated that the bismuth electrodeposition in studied conditions evolves with a three-dimensional progressive nucleation. SEM images show that grain size of bismuth deposits decreases while adopting a well-defined geometry as ammonium salt concentration increases. EDS analysis confirms that pure bismuth thin films were obtained and X-Ray diffraction indicates that the bismuth growth follows a preferential orientation along the (012) reticular plane.

Keywords
Bismuth, ammonium chloride, deep eutectic solvent, electrodeposition, nucleation.

A Facile Synthesis of Iron-Cobalt-Nitrogen-doped CNTs as High Electroactivity Catalysts of Oxygen Reduction Reaction

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Efficient dispersion of M-N-C molecular macrocycles on carbon nanomaterials support is an attractive strategy to noble metal-free Oxygen Reduction Reaction (ORR) electrocatalyst. In recent years, Co phthalocyanine(CoPc) derivatives have been studied as metal complex catalysts for oxygen electroreduction. In particular, CoPc compounds supported with multiwall carbon nanotubes (MWCNTs) have attracted great attention. CoPc is a transition metal macrocycle, and exhibits an unique ORR capability for alternative cathode catalysts, due to its large conjugated molecular structure with strong π-π interactions between aromatic rings.

Compared to most of the studies reported, the synthesis of Fe/Co doped C-N nanotubes in this work is different. Preparation of the catalysts does not involve complex and harsh equipment, and more importantly, it does not need adding pristine carbon nanotubes to raw materials. ,Carbon nanotubes were in situ formed via high temperature pyrolysis of a mixture of CoPc, ferrocene and dicyandiamide. The ORR behavior of Co-Fe-N-doped CNT catalysts is evaluated by employing the rotating disk electrode (RDE) method. Under alkaline conditions, it shows an onset potential of 0.01 V close to that of commercial Pt/C

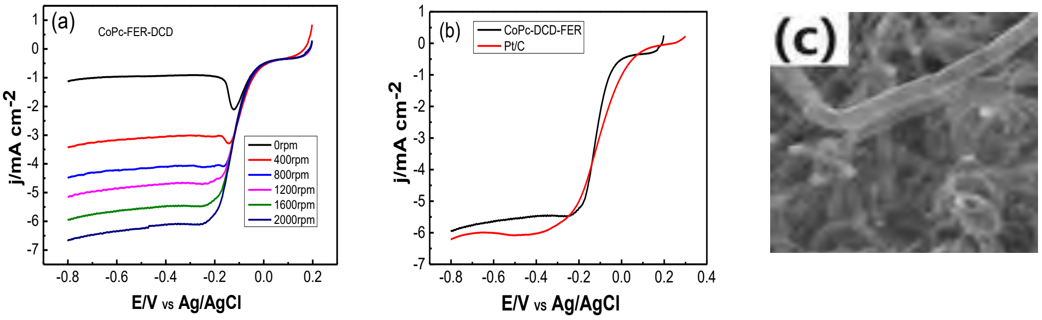

Fig.(a) LSVs of Fe_3Co_1-N@MWCNTs in O_2-saturated 0.1 mol L^{-1}KOH at 5 mV s^{-1};(b) LSVs of the catalysts in O_2-saturated 0.1 mol L^{-1}KOH at 1600 rpm at 5 mV s^{-1};(c) SEM images of Fe_3Co_1-N@MWCNTs.

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A Metal-free N-P Doped Graphene Catalysts for Oxygen Reduction

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The oxygen reduction reaction (ORR) is traditionally carried out with noble metals (such as Pt) or non-noble metals as catalysts. However, these metal-based catalysts often suffer from multiple disadvantages, including high cost, low selectivity, poor stability and detrimental environmental effects. Here, we prepared a non-metallic oxygen reduction catalyst doped with nitrogen and phosphorus via direct heat treatment of a mixture of starch and dicyandiamide, followed by a further heat treatment with the addition of triphenyl phosphorus to get graphene co-doped with nitrogen and phosphorus. Graphene, one-atom-thick layers of sp^2 -hybridized carbon atoms packed in a honeycomb lattice, is now renowned for its fascinating electronic properties. Since phosphorus has a lower electronegativity than carbon, i.e., higher electron-donating ability, it is of great significance to explore the unique properties of phosphorus-doped graphene, which is of great significance in electrocatalyst development.

The ORR behavior of the prepared N-P-doped grapheme catalysts is evaluated employing the rotating disk electrode (RDE) method. Under alkaline conditions, it shows an onset potential of -0.04 V which is higher than many catalysts doped with metals andis close to that of the commercial Pt/C.

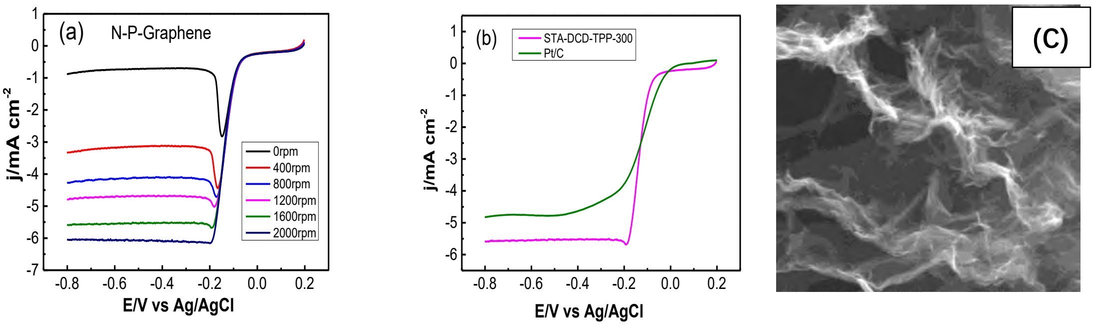

Fig.(a) LSVs of N-P-Graphene in O_2-saturated 0.1 mol L^{-1}KOH at 5 mV s^{-1};(b) LSVs of N-P-Graphene and Pt/C in O_2-saturated 0.1 mol L^{-1}KOH at 1600 rpm at 5 mV s^{-1};(c) SEM image of N-P-Graphene.

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Yttrium Ruthenate Electrocatalyst for Oxygen Evolution Reaction in Acidic Media

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Abstract

With the growing demand for energy and the increasing concerns about environment pollution from fossil fuels, research interest in energy conversion from sustainable energy sources is stimulating and sustaining. Electrochemical reaction can be used to store electrical energy efficiently via chemical bonds. For example, energy can be stored by electrochemically splitting water to form hydrogen and oxygen, whose subsequent recombination can provide clean electrical energy with the only by-product of water. However, the efficiency of hydrogen fuel generation from water splitting is severely limited by the sluggish kinetics of the oxygen evolution. Therefore, an efficient electrocatalyst for the oxygen evolution reaction (OER) is needed to afford high current at low overpotential and improve the energy conversion efficiency. Although Iridium oxide (IrO_2) and ruthenium oxide (RuO_2) are widely recognized as the most active electrocatalyst for OER, the scarcity nature as well as high cost have limited their widely application seriously. Therefore, it is urgent to develop low-cost alternatives as highly efficient electrocatalysts for OER process.

Here, we have prepared a novel kind of pyrochlore $Y_2Ru_2O_{7-\delta}$ electrocatalyst with high activity and stability toward OER in strong acidic media. $Y_2Ru_2O_{7-\delta}$ electrocatalyst shows an ultralow onset overpotential of less than 240 mV in 0.1 M H_2SO_4 solution and stable chronopotentiometric performance under constant current density. This study provides an effective choice for the design of high performance electrocatalyst for water electrolysis.

Fig.1

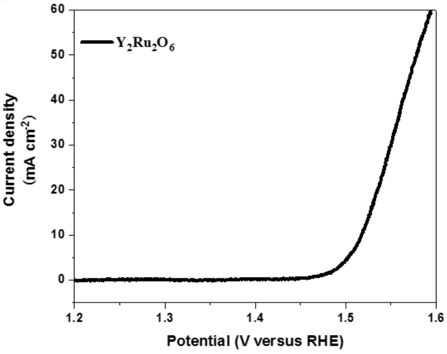

Fig.1 LSV curves of $Y_2Ru_2O_6$

Fig.2

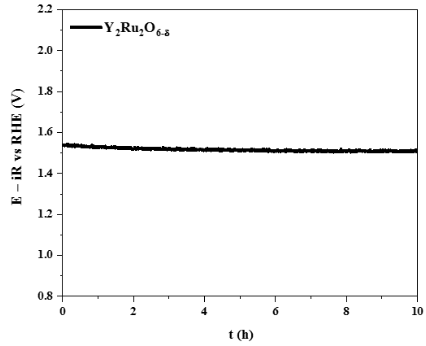

Fig.2 Chronopotentiometry performance under constant current density at 1 mA/cm^2.

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Preparation and electrochemical properties of porous NiCo-MOF from urea dopping

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With the growing of environmental problems, the development of fuel cells and metal-air batteries is becoming more and more important. Oxygen reduction reaction (ORR) is an important and key process for energy conversion and storage systems. Noble metal-based materials, such as Pt and Pd, are still the most efficient catalysts for ORR. Nevertheless, their large-scale applications were hindered by their rarity, high cost and low tolerance to fuel crossover. Therefore, developing highly active and cost-effective catalysts as alternatives for ORR is significant for both practical applications and academic researches.

In this paper, we firstly prepared a bimetallic doped metal-organic frameworks, and then hydrothermally mixed it with urea to obtain the porous product by pyrolysis. The SEM images of the CoNi-MOF are presented in Fig.1.(a,b) and the SEM image of the corresponding CoNi-MOF@Urea is presented in Fig.1(c). Fig.1(d) shows that the CoNi-MOF and CoNi-MOF@Urea had superior catalytic activity for oxygen reduction in alkaline condition. Catalytic activity of CoNi-MOF@Urea for oxygen reduction is close to that of commercial Pt/C.

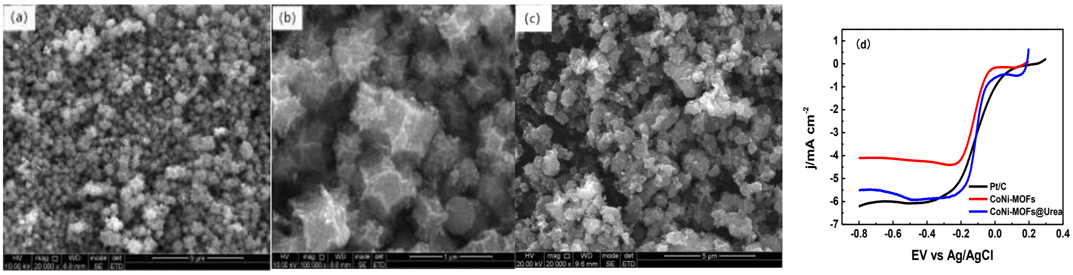

Fig.1.(a,b,c)The SEM images of all preparede catalyst ,(d) The ORRLSV curves for CoNi-MOF, CoNi-MOF@Urea and commercial Pt/C (20 wt %) at a rotation speed of 1600 rpm.

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Co, Fe Codoped Yolk-Shell Hollow Carbon Sphere as an Effective Electrocatalyst for ORR in Alkaline Solution

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Anthropogenic climate change and environmental pollution problem, caused by the booming depletion of fossil fuels, make it urgent to develop renewable energy storage and conversion technologies. Among diverse technologies, metal-air batteries play a significant role for the conversion from chemical energy to electric energy due to their high theoretical power density and environmental friendliness. The cathodic oxygen reduction reaction (ORR) in metal-air batteries is so sluggish in nature that we usually need Pt-based electrocatalysts to accelerate the ORR kinetics for their commercial application, even the metal Pt is extremely precious and scarce. Therefore, exploring electrocatalysts with excellent ORR catalytic activity and stability to replace the Pt-based catalyst is extremely urgent.

Herein, we use the one-pot synthesis method to synthesize a bimetal (Fe and Co) doped yolk-shell hollow carbon sphere using dopamine, cobalt chloride hexahydrate and ferric chloride as carbon, cobalt and ferric source respectively. Results show that the catalyst has an excellent electrocatalytic activity for oxygen reduction reaction (ORR) in 0.1 M KOH solution. The synthesis procedure is shown in Fig.1a, and the linear sweep voltammetry (LSV) curves in 0.1M KOH with a scan rate of 5 mV/s are presented in Fig.1b.

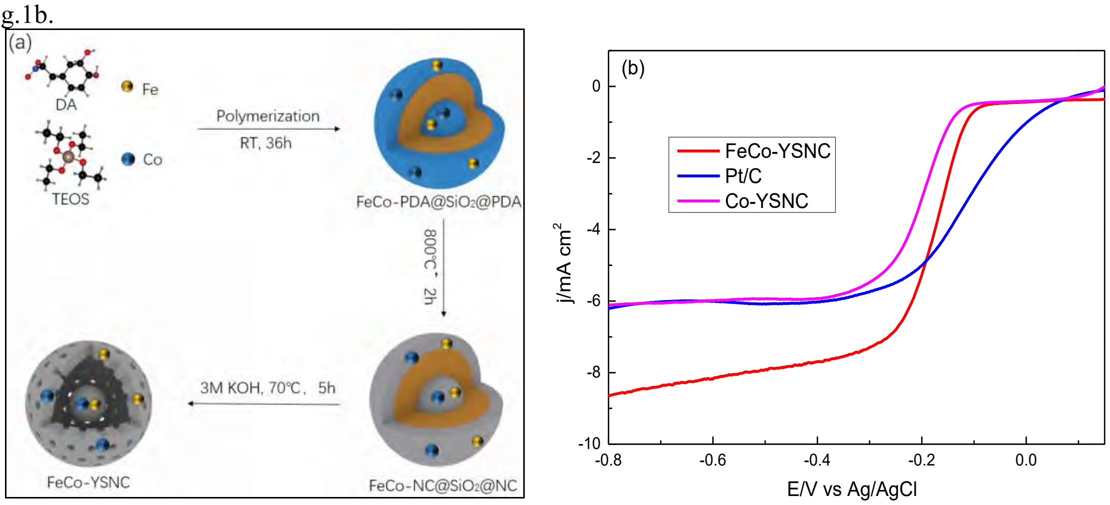

Fig.1. Synthesis procedure of FeCo-YSNC (a) and LSVs of FeCo-YSNC, Co-YSNC and Pt/C at 1600 rpm in 0.1M KOH (b).

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Excellent Oxygen Reduction Electrocatalyst Assembled from Hollow Carbon Spheres and Bamboo-like Carbon Nanotubes

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Economic development and technological advancement are accompanied by increasingly prominent problems of environmental pollution and energy crisis, which has accelerated the inevitable transformation of the energy structure from traditional fossil energy to renewable energy. Oxygen reduction reaction (ORR) plays a key role in renewable energy conservation and storage technologies. Platinum (Pt) and platinum (Pt)-based catalysts are widely considered to be the most effective catalysts for ORR. However, limited by high cost, rare source and declining activity made it in great demand to develop an alternative catalyst to precious metal platinum.

Under this background, we have developed an effective ORR electrocatalyst as shown in Fig.1a and b, which is composed of non-noble metals nickel and cobalt as active materials, assembled from carbon hollow spheres and carbon hollow nanotubes. First, the nickel and cobalt co-doped hollow carbon sphere was prepared by using silica balls as hard template, dopamine hydrochloride as carbon source and nitrogen source. Subsequently, using nickel and cobalt as growth sites, composites from hollow carbon spheres and hollow carbon tubes were prepared. The rotating disk electrode (RDE) measurement was performed to assess the electrocatalytic activities regarding ORR of the prepared catalyst by comparison with commercial platinum carbon.

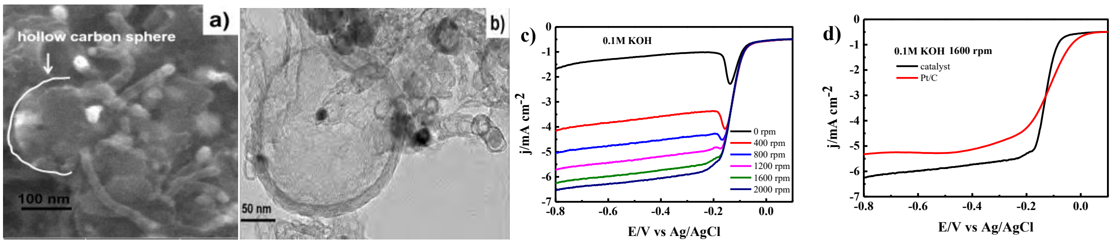

Fig. 1. SEM image of catalyst (a); TEM image of catalyst (b); RDE polarization curves of the prepared catalyst in O_2-saturated 0.1 mol • L^{-1} KOH at different speeds (c) and comparison of prepared catalyst with Pt/C at 1600 rpm (d).

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In situ Observation of Metallic Dissolution and Corrosion Characterization of Ternary CoCrMo Libraries in Simulated Human Body Fluid Environment

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The most important material use in implants for total hip replacement is a cobalt-chromium-molybdenum alloy (known as CoCrMo). The important property which makes this material suitable for implants are: biocompatibility and appropriate strength, stiffness, hardness, and wear resistance, together with high elastic modulus [1]. The composition of this alloys lays in the range of 26-30 at.% Cr, 2.9-4.1 at.% Mo together with other minor alloying elements (C, Si, Ni, Mn) and Co.

In order to investigate a broader compositional range around the composition of bulk CoCrMo, in this work a ternary compositional range from the cobalt, chromium and molybdenum metallic system was obtained by means of co-sputter deposition. Energy-dispersive X-ray spectroscopy revealed a compositional matrix containing Mo (3-10 at.%), Cr (17-48 at.%) and Co (46-79 at.%). The microstructure analysis of respective alloy compositions was undertaken with the help of high resolution scanning electron microscope. A sharp change from spike or conical to a refined grain and compact microstructure was achieved with the increase in Cr content. Higher Mo content was responsible to induce further grain refinement. Crystal structure investigation via X-ray diffraction exhibited weak and broad peaks matching the rt HCP and ht FCC structure of Co at all compositions. Addition of Mo and Cr was responsible by a slight shift in the respective peaks. Electrochemical experiments e.g. open circuit potential (OCP), Tafel extrapolation, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were utilized to examine the corrosion properties of various alloy compositions in Ringer`s solution at 37 ºC. A special flow type scanning droplet cell microscope (FT-SDCM) containing three electrodes setup was utilized to perform the experiments. Furthermore, to study the role of chromium and molybdenum during passive and transpassive dissolution (CV experiments) and ICP-OES was directly coupled with FT-SDCM. To investigate the enrichment or dissolution of a specific metal, the instantaneous dissolution rate of each metal was converted into the normalized dissolution with respect to Co. No considerable passivation was observed at the higher Co content (above 70 at.%) regardless of Cr and Mo concentrations. Active to passive dissolution significantly drops as the Cr content becomes higher whereas, on the other hand increase in Mo content improved the transpassive dissolution above 0.6-0.7 V vs SHE. Alloys in the range of (7-10) at.% Mo (40-48) at.% Cr (complementary Co) show improved corrosion resistance and dissolution which make them suitable for further testing and biomedical application.

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Two Routes for Extracellular Electron Transfer in *Enterococcus faecalis*

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Bacterial electrochemistry is currently a much expanding research field with many fundamental as well as practical implications in e.g., biotechnology and analytical chemistry [1-4]. Most commonly Gram negative bacteria have been investigated, however, also Gram positive bacteria have during the last few years been at focus [4,5]. We have previously shown that the Gram positive lactic acid bacterium *E. faecalis* is a weak electricigen [6] and that both monomeric redox mediators and redox polymers, when added to the system, can largely increase the rate of extracellular electron transfer from the bacterial cells to electrodes [7-10].

In this presentation it will be demonstrated that electrons generated in glycolysis can be transferred to electrodes via two different pathways [11]. The finding is of interest and value to those active in several fields of microbiology, such as environmental, applied, and medical microbiology. Our research results, which are based on molecular genetics, biochemical and electrochemical studies, also contribute to basic knowledge in microbiology and physiology.

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Sustainable electrochemical production of tartaric acid

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The development of green industrial processes has been attracting more attention in the last years and it requires renewable energy sources. Large-scale electrification of the energy and chemistry sectors is a crucial condition for the transition from a society based on fossil resources to a sustainable society based on renewable building blocks. Transformation of CO_2 into chemicals has been intensively studied over the past decades because this molecule can be used as C_1 feedstock in electro-organic synthesis due to its abundant, cheap, renewable and non-toxic nature[3–5]. Of particular interest of this molecule is the synthesis of two- to four-carbon atom products (C_2-C_4). Concerning the synthesis of C_2-C_4 products, tartaric acid (TTA) attracts attention because it is an important product used in the textile printing, dyeing, pharmaceutical and food industries[11]. In the past years, the price of TTA and its salts has varied as much as 50 %, as might be expected when the source of the raw material is a by-product of another industry.

Herein we describe a study of the electrochemical reduction of oxalic and glyoxylic acids towards a feasible green and sustainable production of tartaric acid in aqueous and/or acetonitrile solvent using silver and lead electrodes.

Our results show that on the silver electrode, for both oxalic acid and glyoxylic acid, the reduction reaction is more favorable towards the dimerization step, leading to tartaric acid, due to the increase in the local pH, while on the lead electrode the step involving the protonation of the intermediate is more favorable, leading to the formation of glycolate.

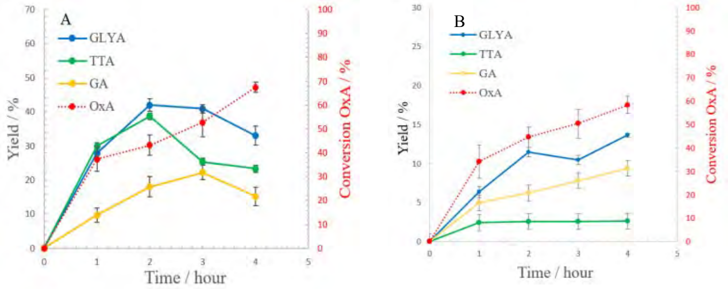

Figure 1. Calculated yield and conversion of OxA and the main liquid products detected by HPLC on Ag (A) and Pb (B) electrodes in ACN solution + 0.1 M TEACl + 0.1 M OxA.

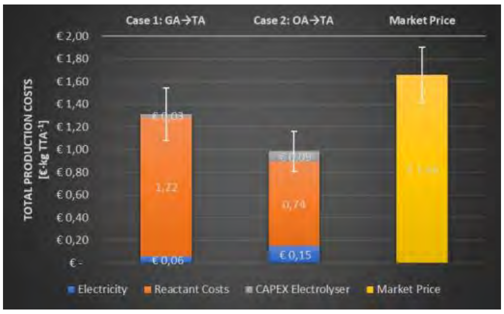

Figure 2. OPEX, CAPEX and Total Production Costs for TTA for Case 1 (from GLYA) and Case 2 (from OxA), and Market Price for TTA from vendors.

Techno-Economic Analysis shows that tartaric acid production from glyoxylic acid and from oxalic acid via electrochemical synthesis can be a potential process at industrial scale. In the present case, the oxygen evolution reaction was chosen as the reaction at the other electrode for practical reasons, but oxygen is a low-value product. Another anodic reaction with a more valuable oxidation product can be selected to increase the profitability of the overall electrochemical process, and thereby decrease the total production costs of tartaric acid.

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Amorphous Nanocluster PtNiP supported on Defective Graphene as an Efficient Electrocatalyst for Methanol Oxidation Reaction

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Pt based materials with high specific surface area have attracted increasing attention as a result of their high activity and durability for electrocatalysis, because of their high surface area, more active sites and high electrical conductivity.[1, 2] Herein, amorphous PtNiP/graphene nanoclusters were successfully prepared by a simple process that hypophosphite-assisted co-reduction method to electrocatalyze methanol oxidation. The diameter of PtNiP/graphene nanoclusters was about 0.92 nm. The morphology and structure of PtNiP/graphene nanoclusters were characterized by transmission electronic microscopy and x-ray photoelectron spectroscopy. Benefiting from the size-confined growth mechanism and the doping of P, PtNiP nanocluster was anchored uniformly with controllable size on the surface of graphene. Meanwhile, P was used to form PtNiP alloy and adjust the electronic structure of Pt. The as-prepared PtNiP/graphene catalyst exhibits excellent mass activity as high as 826.1 mA•mg$^{-1}_{\text{Pt}}$, which is 2.58 times higher than commercial Pt/C and excellent durability after 1000 cycles CV test.

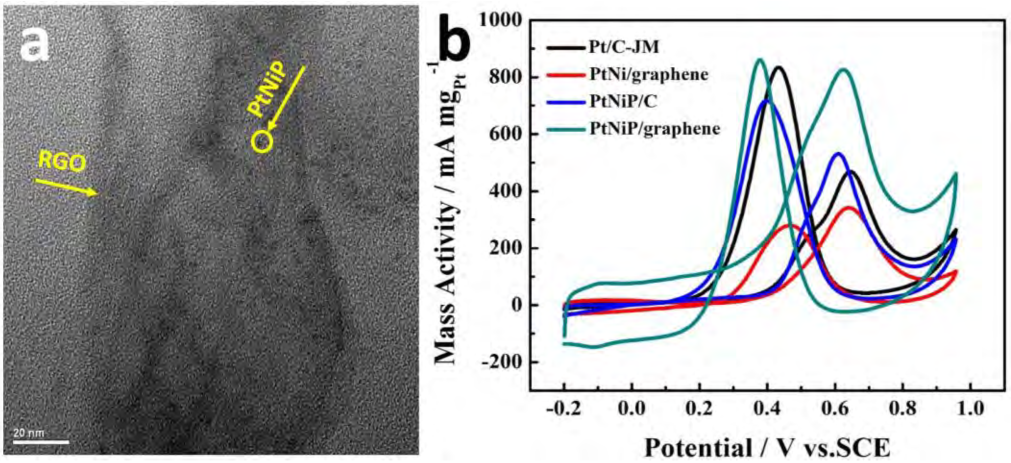

Fig.1. (a) TEM image of PtNiP/graphene. (b) MOR curves recorded at room temperature in a 0.5 M H_2SO_4+1 M CH_3OH aqueous solution at the scan rate of 50 mVs^{-1}

Acknowledgments

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Highly active and stable nanoporous RuO_2 catalyst to oxygen evolution reaction in acidic media by advancing micro/mesoporous structure

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Nanoporous RuO_2 is very promising to achieve the activity and stability of electrocatalyst for oxygen evolution reaction (OER) in acidic medium, but it is still challenging[1]. This article reports a nanoporous RuO_2 catalyst with high catalytic performance in acid OER. The RuO_2 catalyst is prepared by a simple and effective ammonia-induced pore formation method, which has a large number of micropores/mesopores. As a self-supporting electrocatalyst, the nanoporous RuO_2 has excellent acid OER activity. The overpotential at 10 mA cm^{-2} is 215 mV. More importantly, the overpotential difference of the OER of this catalyst before and after accelerated stability testing was only 35 mV, and it did not show significant deactivation or decomposition. Therefore, the catalyst can be used as an efficient OER electrocatalyst in acidic media.

Fig. 1

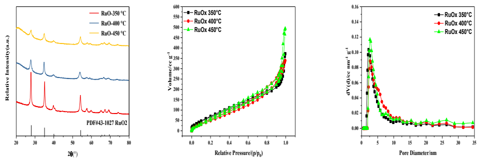
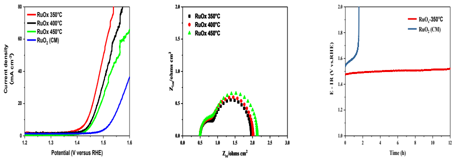


Fig. 2



Acknowledgements

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Advanced Filter Membrane Separator for Aqueous Zinc-Ion Batteries

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Aqueous zinc-ion batteries with low cost and inherent safety are considered to be the next-generation energy storage device. However, it is suffering from poor cycling stability and low Coulombic efficiency caused by the serious zinc dendrites during the cycling. In this work, a porous water-based filter membrane is firstly proposed as separator due to its good toughness and uniform pore distribution. Compared with conventional cells with glass fiber separator or filter paper, the cells with filter membrane show a longer cycle life. The results demonstrate that the symmetrical cell using a filter membrane can cycle over 2600 hours with a low voltage hysteresis of 47 mV. Moreover, aqueous Zn//$NaV_3O_8 \cdot 1.5H_2O$ cell based on the filter membrane is constructed, which demonstrates a high capacity retention of 83.8 % after 5000 cycles at 5 A g^{-1}. The mechanism research results reveal that the excellent dendrites inhibiting the ability of the filter membrane should be attributed to its uniform pore distribution rather than its composition. This work proposes a filter membrane separator and reveals the great influence of separator on the zinc stripping/plating process, which will shed light on the development of high-performance aqueous zinc-ion batteries.

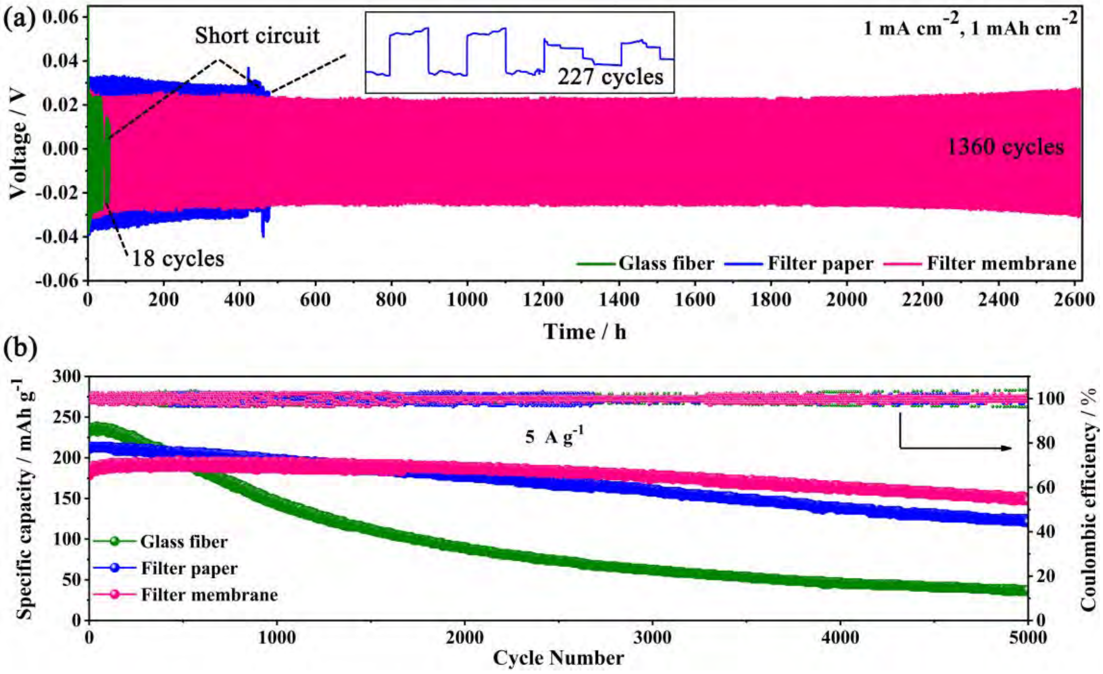

Figure. The cycling performance of cells with different separators. (a) Zn//Zn symmetrical cells at the current density of 1 mA cm^{-2} with areal capacity of 1 mAh cm^{-2}. (b) Zn//$NaV_3O_8 \cdot 1.5H_2O$ full cells at 5 A g^{-1}.

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$Ti_3C_2T_x$ modified graphene foam as a lightweight interlayer for improved lithium-sulfur battery

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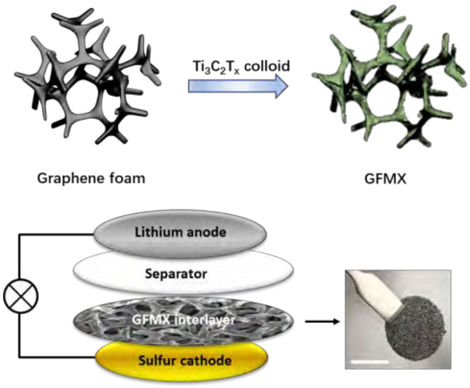
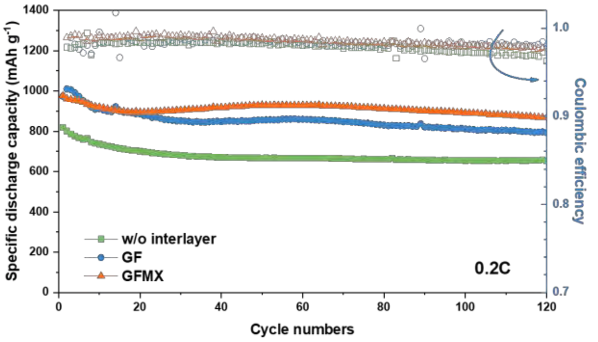
Lithium-sulfur (Li-S) batteries have high specific capacity and energy density overweigh the commercial lithium ion batteries [1]. Besides, the elemental sulfur also surpasses other cathode materials for its low-cost, natural abundance and environmental benignity [2]. Nevertheless, Li-S batteries still have several crucial drawbacks: the poor electrical and ionic conductivities of sulfur species seriously retard the redox reaction. In addition, the so called "shuttle effect" brought by the dissolution of polysulfides can degrade the capacity and stability performance [3]. To overcome these obstacles, one special strategy is to build a functional interlayer between the cathode and the separator [4]. Here, the highly conductive lightweight graphene foam (GF) was modified by the $Ti_3C_2T_x$ (MXene) colloid and the resulted GFMX interlayer inherited their merits as lightweight and polysulfide-attractive. With this GFMX interlayer, the cell presented 867 mAh g^{-1} after 120 cycles with 88.8 % retention, which exceeds the pristine one's capacity by 32.8 %.





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Stabilized Pt Cluster Based Catalysts Used as Low-loading Cathode in PEMFC

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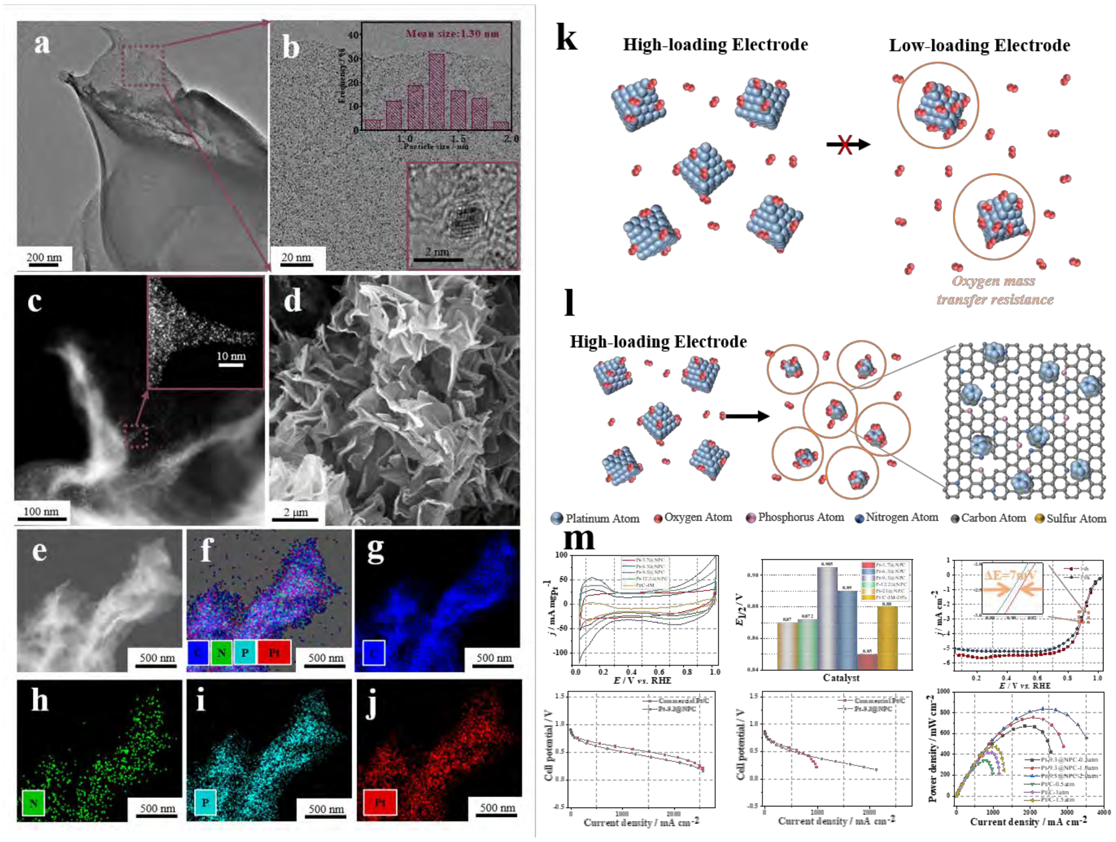
Lowering the Pt catalyst loading in fuel cell cathode without sacrificing the cell performance remains topical for fuel cell development, which will largely reduce the capital cost of the technology. This, in the meantime, is also highly challenging, since lowering the Pt loading not only reduces the overall kinetics of oxygen reduction reaction (ORR), but also causes serious mass transfer issue in high current density domain (HCD). Herein we overcome this difficulty by obtaining a highly active and stable Pt cluster based catalyst, where the catalyst loading reduction is completely compensated by the extraordinarily high electrochemical specific area (358.6 m^2 g_{Pt-1}) and the high dispersion of the platinum clusters. The Pt clusters, with average size of 1.3 ± 0.4 nm and atomic ultization rate up to 32.81%, are highly stabilized due to the strong anchoring effect of the N, P doped carbon nanosheets. As a result, the final Pt-9.3@NPC catalyst not only outcompetes the commercial Pt/C catalysts in terms of activity, but is also more stabilized during potential cycling. Even further, the cell assembled using Pt-9.3@NPC as cathode catalyst (0.1 mg_{Pt} cm^{-2}) conveys much higher fuel cell performance (837 mW cm^{-2}) in H_2/Air mode than the counterpart commerical catalysts (472 mW cm^{-2}), clearly evidencing the success in surmounting the mass transfer problem.



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Ecological and economical stationary energy storage system based on aqueous zinc-ion batteries

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The replacement of fossil energy sources by wind and solar power is dependent on ecological and economical large scale energy storage solutions such as pumped-storage, hydrogen and batteries. Besides established systems such as lead-acid, Ni-MH and Lithium-based systems, additional emergent electrochemical systems are needed to satisfy increasing demand.

In the conventional zinc-ion battery (ZIB), an energy-dense metallic zinc anode (820 Ah/kg; 5854 Ah/l) is combined with an aqueous electrolyte ($ZnSO_4$) and preferably with a δ-MnO_2 cathode (308 Ah/kg) to form an environmentally benign, non-toxic, non-flammable and low cost battery (<50 €/kWh). Most battery components are readily available as raw materials as well as high quality commercial products. Recycling processes for zinc and partially for MnO_2 are established. All ecological concerns are addressed within this battery chemistry. Thus, remaining economical and technical challenges are cycling stability of the ZIB and its scale-up to commercially available battery formats. The increasing amount of ZIB publications indicates the potential of this highly promising battery chemistry. Multiple studies were able to achieve a high electrochemical stability by demonstration of 1000-8000 charge/discharge cycles. [1,2] However, these results have been achieved in coin cell design containing low amount of active material and have not been demonstrated in larger battery formats yet.

This work aims at developing a prismatic ZIB cell and electrode manufacturing based on aqueous inks excluding the toxic and expensive NMP solvent. After establishing a homogeneous and stable ink composition, the electrodes were coated and tested first in coin cell design. Hereby, MnO_2 capacity of 300 mAh/g at a loading of 5 mg/cm² and current density of 60 mA/g (C5) was achieved that is close to theoretical value. Furthermore, we studied influence of the electrolyte composition on corrosion of the zinc anode (H_2 evolution), MnO_2 dissolution/deposition as well as battery component stability. Corrosion experiments in 1 M $ZnSO_4$ at 80°C for 8 weeks have been performed for commercially available passive and active cell components, such as binders, separators, current collectors, cell casings and gaskets. Conventional current collectors such as aluminum and copper underwent complete decomposition or severe corrosion. Stainless steel components (1.4404, 1.4310), titanium and others demonstrated very high corrosion stability.

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Eco-friendly Chitosan: Anticorrosion Film on aluminum alloy 6061 Via a Facile Method of Pyrolysis

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As an environmentally friendly multi-carbohydrate material, chitosan contains a great amount of amino and hydroxy functional groups in the molecular structure. A highly corrosion-resistant carbon film doped nitrogen was successfully prepared on the surface of aluminum alloy 6061 (AA 6061) by pyrolysis. Corrosion behavior of the as-prepared film was studied via EIS, Tafel polarization curve and equivalent circuit in 0.5 M H_2SO_4 and 2 ppm HF. The corrosion current density of carbon film on AA 6061compared that of bare AA 6061 was down dramatically from 8.356×10^{-5} $A\cdot cm^{-2}$ to 7.461×10^{-8} $A\cdot cm^{-2}$,which reveal good corrosion resistance. The surface morphology and composition were characterized by field emission scanning electron microscopy (FE-SEM) and its affiliated energy dispersive spectrometer (EDS), atomic force microscope (AFM), X-ray diffraction (XRD), Raman spectrum, fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS), respectively. The results illustrate that the as-prepared film on AA 6061 was a nitrogen-doped graphitized carbon film and exhibited a very high protection inhibition of 99.91%.

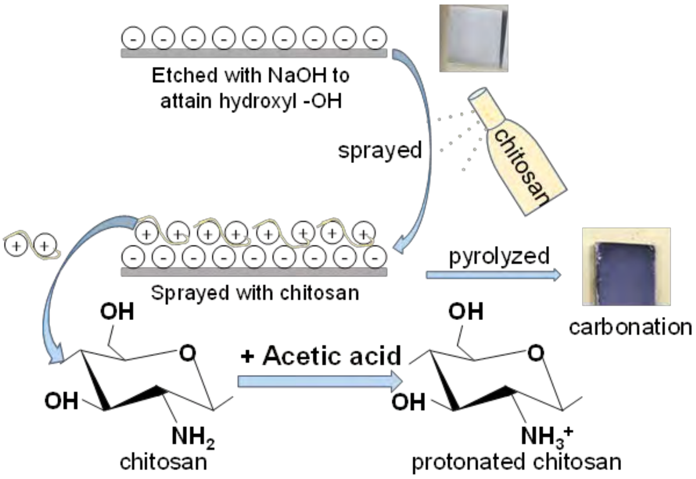

Fig. 1 The schematic diagram of the experimental process

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Strategy to provide hydrogen by formic acid decomposition

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The dehydrogenate splitting of formic acid (FA) offers an ideal solution to H_2 storage and on demand releasing in a mobile fuel cell, where catalysis is at the heart of efficient hydrogen delivery. Lack in fundamental knowledge on catalytic interface has bottlenecked the design and development of effective catalysts with both high conversion efficiency and selectivity. In our recent work, we present our effort to understand the nature of active sites for the Pd catalysts,[1] based on which the relationship between the concentration of the substrate and the performance has been discussed. Here we propose that the saturated formate solution with few formic acid could keep the catalyst stay in the best performance, which could make the hydrogen produced longer and faster if the formic acid could be supplied in the same rate.

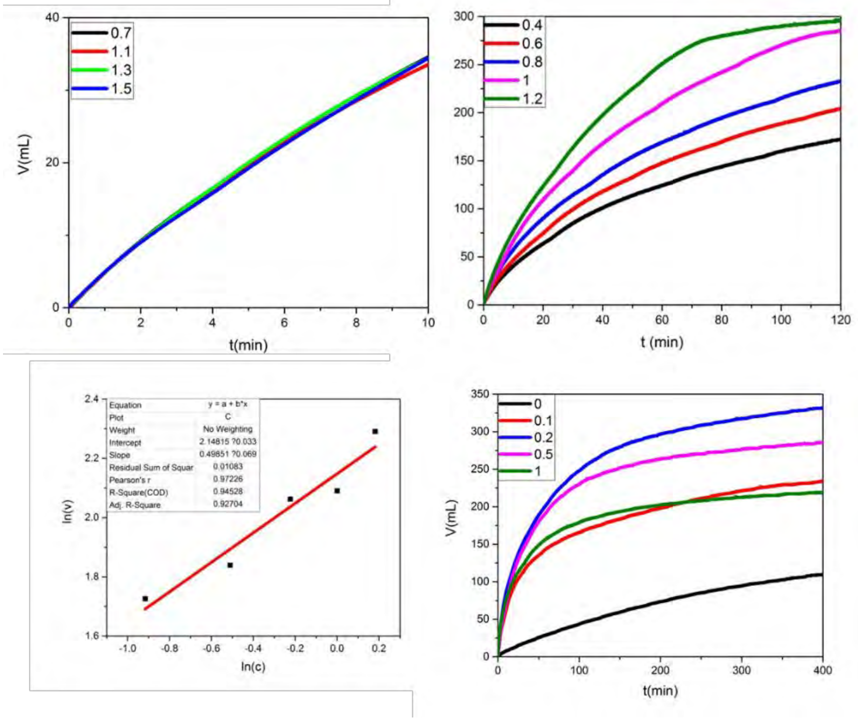

Fig.1 Relationship between the activity and the substrate, (a) HCOOH-Pd/C, (b) HCOONa-Pd/C, (c)linear relationship in (b), and(d) performance in the saturated formate solution with few HCOOH.

Acknowledgements

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Synergistic engineering of MoS_2 via dual-metal doping strategy towards hydrogen evolution reaction

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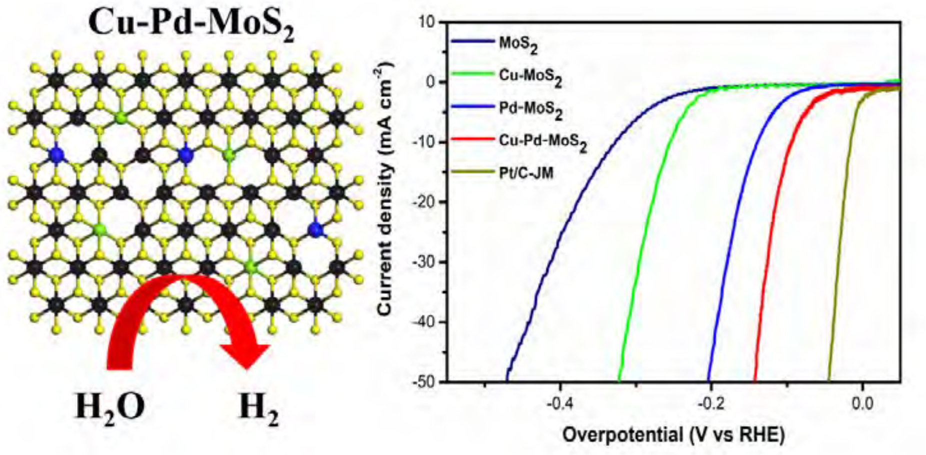
Hydrogen is an ideal energy carrier to replace the conventional energy based on fossil fuels, where its high efficiency production constitutes the cornerstone of the sustainable hydrogen economy.(*1, 2*) Currently, the cathode reaction, i.e., the hydrogen evolution reaction (HER) process relies heavily on platinum-based materials, thus impeding the water electrolysis from wide spread application, due to the scarce and high price of Pt.(*3*) Molybdenum disulfide (MoS_2) is reckoned as one of the most positive low-cost HER catalysts to replace platinum-based precious metals in acid media.(*4*) Unfortunately, some issues preclude MoS_2 from being truly applicable including limited active sites, poor conductivity and lack of intrinsic activity.(*5*) Herein, we report a Cu, Pd co-doped MoS_2 nanomaterial as an efficient and stable HER electrocatalysts, which partially resolve the above-mentioned problems and leads to high overall performance. Specifically, we improve the electric conductivity of the MoS_2 by Cu dopant and realize the phase transition of MoS_2 from pristine 2H phase to stable 1T phase by Pd dopant. More importantly, we increase active site density to facilitate fast electrocatalytic Faradaic process via synergistic effects of Cu and Pd doping, and tune electronic energy states of MoS_2 to improve HER intrinsic activity. In acidic media, the performance of Cu-Pd-MoS_2 catalyst in terms of a low overpotential (-93 mV) at 10 mA cm^{-2}, a small Tafel slope of 77 mV dec^{-1}, and an excellent stability is better than that of single-doped catalysts.



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5.H. Jin *et al.*, Emerging Two-Dimensional Nanomaterials for Electrocatalysis. *Chem Rev* **118**, 6337-6408 (2018).

Unexpected High Activity of Nanostructured Rh-Pt Catalysts for Ethanol Electrooxidation

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Ethanol electrooxidation reaction (EOR) proceeds via a multistep process. Platinum is a good electrocatalyst for the first electro-oxidation step, in acid medium, the adsorption of ethanol is followed by platinum catalyzed dehydrogenation. However, platinum is poor electrocatalyst for ethanol C–C bond break. The last step is the adsorbed CO electro-oxidation to CO_2. Hence, the strategy to enhance the rate of the last elementary oxidation step is to combine platinum with a second metal, specially an oxophilic metal. While Pt_1Rh_1 alloy nanodendrites exhibit superactivity for EOR [1], rhodium alone is a non-active catalyst. Nonetheless, sub-monolayers of Pt (up to 5 %) onto Rh single crystal surface, showed an unexpected enhancement in the activity and the stability of the EOR [2]. Inspired in the excellent performance of rhodium/platinum, bimetallic nanostructured catalysts were synthesized on carbon-dispersed (Black Pearls 2000®-Cabot Corp.) using chemical reduction from metal precursors achieving low Pt content (in mass) compared to Rh ($Rh_{27\%}Pt_{4\%}C_{69\%}$, $Rh_{27\%}Pt_{6\%}C_{67\%}$, and $Rh_{27\%}Pt_{9.5\%}C_{63.5\%}$), and dispersed pure Pt ($Pt_{5\%}C$ and $Pt_{50\%}C$). TGA/DSC scans in air atmosphere from 30 to 1000°C confirmed the Rh and Pt percentages in the nanoparticles. The XRD results indicated the formation of alloyed polycrystalline Rh and Pt nanoparticles [1]. Also, from the Debye-Scherrer equation [1], for the (111) XRD peak, crystallites of ca. 3.8 nm size were calculated for all samples. From HR-TEM images were observed well-dispersed ≈ 5 nm (sphere-like) nanoparticles. Cyclic voltammetry was performed in 0.5 M H_2SO_4, in the presence and absence of ethanol, in a potential range of 0.05 – 1.10 V (RHE), at 50 mV s^{-1}, the 50th cycle was recorded for all electrodes. The main processes observed in the absence of ethanol were hydrogen adsorption/desorption and formation/reduction of metal oxides. In presence of ethanol (0.5 M), it was possible to observe that small amounts of Pt ($Rh_{27\%}Pt_{9.5\%}C_{63.5\%}$) presented an onset potential, in the first cycle, of 0.39 V and 0.50 V for RhPt and Pt/C, respectively. A high non-normalized activity, 1.93 mA (RhPt) and 1.01 mA (Pt/C) at 0.6 V (RHE), were observed. During the subsequent scans, the RhPt electrodes demonstrated a progressive increase in the anodic and cathodic oxidation current densities whereas the Pt/C remains the same or diminishes in the case of $Pt_{5\%}C$. This fact is so interesting, once the low Pt load embedded in Rh was capable to promote an unexpected and superior EOR result, even if the major component (Rh) is inactive. Thus, the low amount of Pt facilitated the ethanol electrooxidation reaction probably by a bifunctional surface during cycling, achieving the best active site configuration without any performance decreasing of these electrodes cycle to cycle [2]. Additionally, from the distance determination between crystallographic planes by HR-TEM, it is possible to suggest that the lattice strain effect associated with the bifunctional surface effect are responsible for the unexpected high catalytic performance of the RhPt nanoparticles.

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Ti-Doped RuO_2 as Highly Active Acidic Oxygen Evolution Reaction Catalyst

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Though solid polymer electrolyte (SPE) water electrolysis hold the promise in the field of clean energy conversion and utilization, the sluggish anodic oxygen evolution reaction (OER) is the bottleneck for its large overpotential[1]. Herein, we present a Ti doped RuO_2 catalyst with a highly active Ru-O-Ti structure. Attribute to the electron withdraw effect of Ti, Ru in the Ru-O-Ti possess a higher charge density compared with the Ru-O-Ru structure in the undoped one, which can significantly promote the potential determine step of OER on RuO_2 according to the traditional adsorption evolution mechanism (AEM)[2]. Thanks to this unique structure, our best catalyst needs only a low overpotential as 159 mV to reach a current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 electrolyte. Besides, the stable Ti species introduced can work for a long time with only a small amount of dissolves (2.42 % dissolution of Ti after 30 h chronopotentiometry tests at 10 mA cm^{-2}). Full water splitting test imply that a voltage as low as 1.42 V is required to deliver 10.0 mA cm^{-2} for the electrolysis assemble, which is significantly superior to the full cell with bare IrO_2 as anode. We argue that the Ru-O-Ti structure unit introduced by trace Ti doping are responsible for the exhibited superior OER activity.

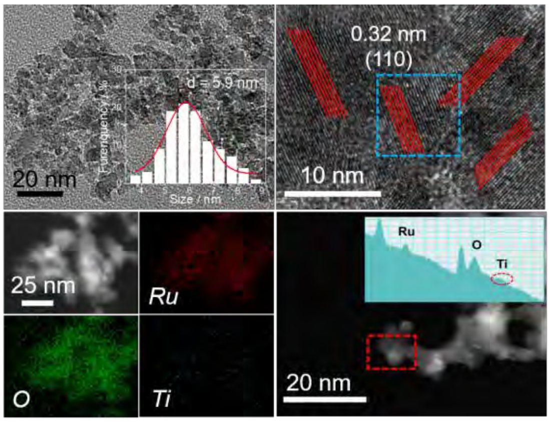

Figure 1. TEM characterization of Ti-doped RuO_2.

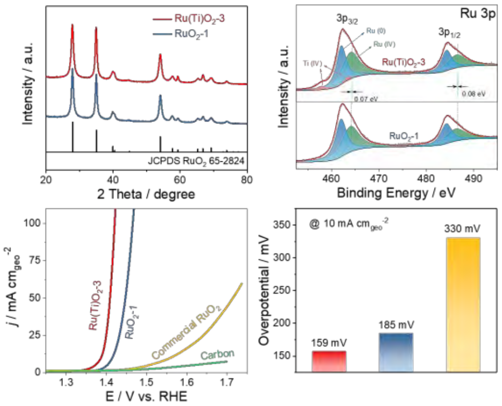

Figure 2. XRD, XPS and electrochemical test results of the Ti-doped RuO_2.

Acknowledgements

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Atomically dispersed Platinum on phosphomolybdic acid and oxidized graphene interface towards HER

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Hydrogen energy technology with hydrogen as an energy carrier is gaining more and more attention due to its advantages such as non-pollution and high energy density(*1*). Among them, hydrogen evolution reaction is one of the cleanest and most sustainable hydrogen production technologies, as a necessary prerequisite for the future economic development of hydrogen energy(*2*). However, its development is subject to the expensive price of precious metals. One of the ideas is to reduce the loading and increase the atomic utilization rate. Single-atom catalyst is the limit that can be reached at present-the theoretical atom utilization rate 100%-so that each metal site can adsorb H atom and produce hydrogen(*3*). Here, we use phosphomolybdic acid with varying valence effect as a soft reducing agent to reduce Pt(IV) to monodisperse Pt atoms. With the increase of the strong reducing agent $NaBH_4$, the low-valence Mo increase, so there is a greater probability of reducing Pt(IV). Through high-resolution transmission electron microscopy and mapping, it can be determined that Pt exists in monodisperse form. PMA and GO construct an interface that is easy to load with Pt, which greatly improves the stability of the catalyst. Although the overpotential is still not as good as JM-Pt/C-20%, its mass specific activity is dozens of times.

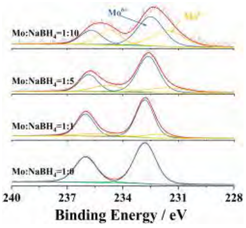

Fig.1 XPS of Mo

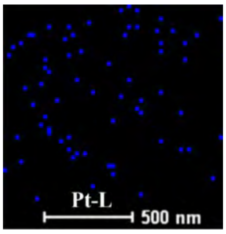

Fig.2 Mapping of Pt

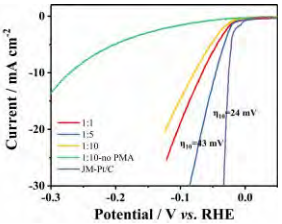

Fig.3 Electrochemistry performance

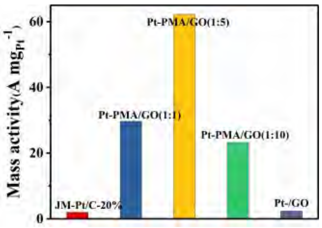

Fig.4 Mass activity

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Defects Control in a Novel Gadolinium Doped Iridium Oxide Catalyst for Acidic Oxygen Evolution Reaction

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Doping the second metal into iridium oxide offers great opportunities for an efficacious regulation of electrocatalytic activity and stability for oxygen evolution reaction (OER).[1, 2] Here, a novel kind of Gadolinium-doped IrO_2 catalyst with high specific surface area and lots of defects is synthesized by a simple template-free ammonia complex-based method. For 5%-Gd-pIrO_2, the overpotential to achieve 10 mA cm^{-2} is only 287 mV and this catalyst exhibits excellent stability under operating conditions. The exceptional performance is derived from its decreased remarkably crystallinity, abundance electronic defects of iridium and oxygen vacancies controlled by two charge compensating mechanism, boosting the kinetics of oxgen evoluction reaction. We believe this strategy can be extended to multifarious material systems for creating defects in nanoparticles.

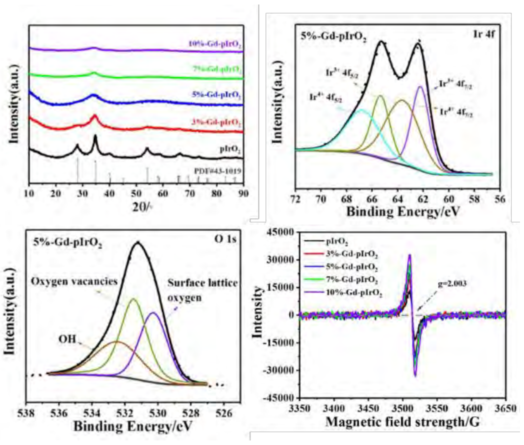

Fig.1 The structure characterization of doped and undoped samples.

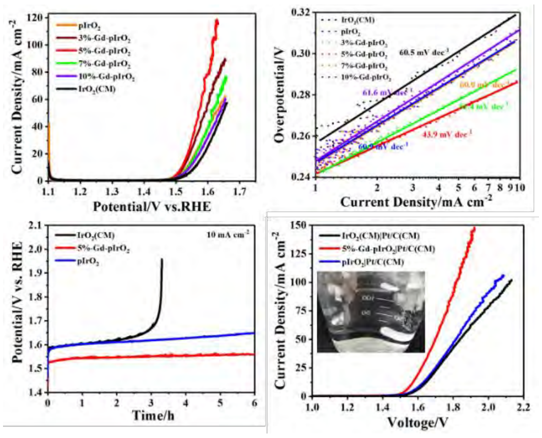

Fig.2 The electrochemical catalytic properties of doped and undoped samples in 0.5 M H_2SO_4.

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Diagnose the contamination effect at the cathode of the PEMFC using Impedance Spectroscopy

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In order to improve proton exchange membrane fuel cell (PEMFC) performance and to increase the cell's lifetime, it is necessary to examine the operation of a PEMFC for analyzing performance losses especially the contaminant effect in the different processes inside the fuel cell with suitable techniques. The AC impedance technique, also known as electrochemical impedance spectroscopy (EIS), is a powerful nondestructive technique utilizing in PEMFC studies. In this study, propene at a concentration of 100 ppm as the contaminants were used in the cathode to study the contamination effect in PEMFC. Disregarding the current direction, the redox reactions of propene only account for at most 0.2 % of the total current at the cathode. Using an EES, we illustrated the contamination effect in terms of influence at both R_{ct} and R_c. This work has the great effect on helping use EIS to examine the PEMFCs. [1-2]

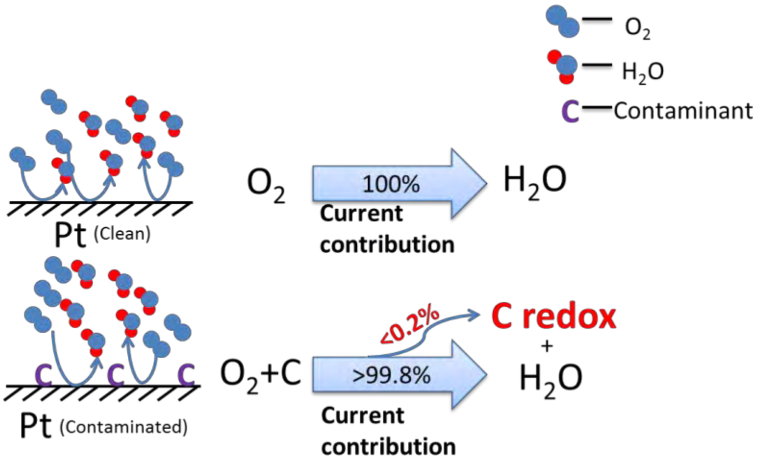

Figure 1. The contamination behavior of Propene at the Pt electrode.

Acknowledgements
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Effect of micropores and chloride ions on Ru / C catalyst for hydrogen evolution reaction

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The hydrogen-energy society demands a cheap and stable production of hydrogen in which highly-efficient electrocatalysts are of paramount importance. The Ru is cheaper while generally displays inferior performances compared to state-of-the-art Pt for hydrogen evolution reaction (HER). Herein, we discover controlling content of Cl^- can decrease toxic effect on Ru/C catalyst and the ration micro/mesopores can avoid the agglomeration of Ru, which is beneficial to increase performance for HER. We prepared Ru/C catalyst with ruthenium chloride and acetylacetonate, and found that ruthenium acetylacetonate has better performance. The catalyst prepared with ruthenium trichloride washed with ammonia water has 18 mV performance improvement. Therefore, it is concluded that Cl^- does have toxic effect on Ru/C catalyst, and it can be eliminated by high temperature or ammonia water washing; the appropriate proportion of the micro mesopores can avoid the aggregation of Ru, be beneficial to the performance improvement for HER.

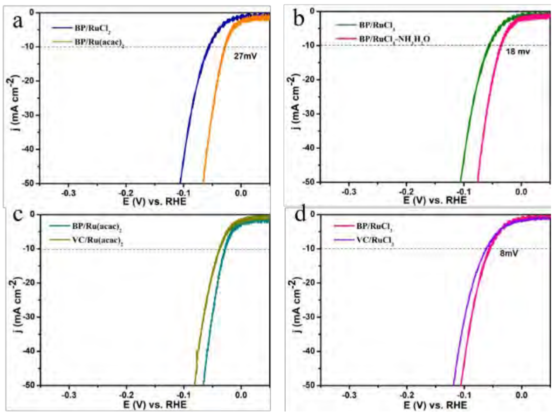

Fig.1 HER polarization curves of Ru/C, (a) different metal sources, (b) Ru/C of after ammonia water washing, (c) and (d) different carbon carriers from the same metal source.

Acknowledgements

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Hybrid high-concentration electrolyte significantly strengthens the practicability of alkaline aluminum-air battery

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Alkaline aluminum-air batteries show great potential for energy storage applications because of their high theoretical energy density and low cost. However, they are suffering from severe anodic self-corrosion and the gelation of electrolyte which greatly reduce the practical energy density and shelf life. Herein, we firstly construct an efficient high-energy alkaline Al-air battery based on high-concentration potassium acetate-potassium hydroxide electrolyte and prototype optimization. The self-corrosion of Al anode is greatly suppressed owing to the special hydrate structure in such electrolyte. The Al-air battery with optimum electrolyte demonstrates remarkable increased discharge capacity of 2324 mAh g^{-1}, and the constructed miniaturized Al-air battery enables an outstanding system energy density of 436.1 Wh kg^{-1} (compared with 85.8 Wh kg^{-1} of normal electrolyte) after integrating a discharge product removing system. This work opens up a new direction for the practical realization of high- energy, low-cost, and high-efficiency alkaline Al-air battery and other aqueous metal-air batteries. [1-4]

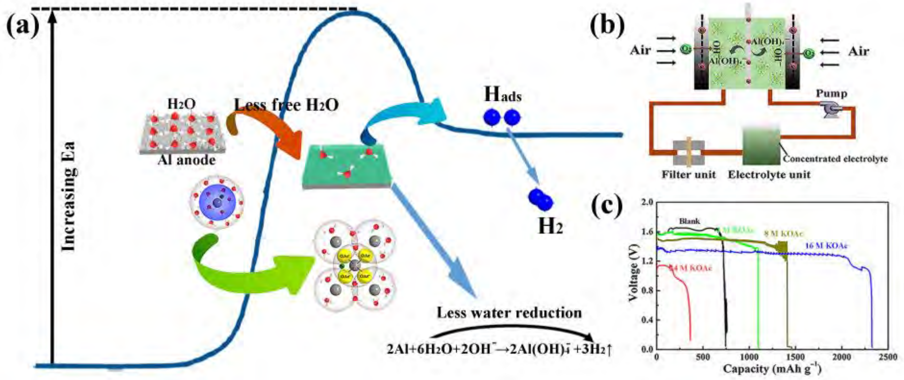

Figure 1. (a) Schematic illustration of the difference of water reduction reaction from 4 M KOH electrolyte to 16 M HCPA-KOH electrolyte. (b) Schematic application diagram of the Al-air battery integrated system. (c) Galvanostatic discharge curves of Al-air full batteries with different electrolytes at a current density of 25 mA cm^{-2}.

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Revisiting Electrocatalysis of Acetaldehyde Oxidation Reaction with Wide Frequency ATR Surface enhanced IR Spectroscopy

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The adsorption and reaction of acetaldehyde on Pt electrode is of considerable interest in surface chemistry and electrocatalysis, since acetaldehyde is either an intermediate or a reaction product of ethanol oxidation reaction (EOR) or the anode reaction in direct ethanol fuel cells. The in-depth mechanistic understanding of acetaldehyde adsorption and oxidation on Pt electrode is essential for further revealing the mechanism of more complicated EOR and developing relevant efficient catalysts.[1]

For decades, owing to the application of in situ IR spectroscopy with either external (IRAS) or internal (ATR) reflection mode, it has been suggested that two pathways may be involved in the acetaldehyde oxidation reaction (AOR) on Pt surface in acidic media, that is, the minor C1 pathway leading to the production of CO2 and the dominant C2 pathway to acetic acid. The C1 pathway involves the C–C bond cleavage to form COads and CHx surface species at low potentials, followed by their further oxidation to CO2 at high potentials. The C2 pathway may proceed via the oxidation of surface C1 intermediates before forming acetic acid. Despite the above general consensus, details regarding AOR on Pt electrode yet remains controversial, in terms of chemical identity and configuration of surface C2 intermediates.

Recently, thin and micromachined Si wafers, designed as internal reflection elements (IREs) for attenuated total reflectance infrared spectroscopy, were adapted to serve as substrates for electrochemical ATR-SEIRAS by Burgess' group.[2] The 500 μm thick wafer IREs with groove angles of 35° are significantly more transparent at long mid-IR wavelengths as compared to conventional large Si hemisphere IREs. In this work,[3] in situ ATR-SEIRAS technique incorporating a micro-structured Si wafer window, p-polarized infrared radiation and isotope labelling is extended to revisit acetaldehyde electro-oxidation on Pt electrode in acid media. New spectral features in the fingerprint region are detected, including the γ(C-H) at 1078 cm-1 and the νas(C-C-O) at 913 cm-1 for adsorbed acetaldehyde and the δ(O-C-O) at 689 cm-1for adsorbed acetate, besides the other enhanced and clearly discriminated spectral signals at higher frequencies. The ATR-SEIRAS measurements together with new DFT calculations incorporating the coadsorption of CO and C2 species enable to clarify the structures and roles of the C2 intermediates ((η1(C)-acetyl and η1(H)-acetaldehyde) during acetaldehyde electro-oxidation.

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Microelectrode Arrays for Biosensing in a 3Dimensional Cell Culture Scaffold

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Microelectrode Arrays (MEAs) were introduced in the 1950s[1,2] and from that moment they are used as a basic tool in electrophysiology, yet their applications for analysis of other types of cell activities is till now rather unexplored. When incorporated in a 3D cell culture scaffold, MEAs provide an adaptable platform for sensing and biosensing of normal cell metabolism; they can also be a convenient tool for recording and simultaneously stimulating electrical activities of a neural network.

Our objective is to develop a novel device that incorporates MEAs in a 3D cell culture scaffold. The device will allow visualizing the gradients and cellular functions inside the cell culture during its growth with the help of MEAs that act as a cell-electrode interface. MEAs will be employed in a cell culture for viability tests through analysis of glucose and oxygen consumption. They will also be used for the investigation of neurotransmission through recording of dopamine and glutamate levels in various points of a neural culture.

The current focus is the fabrication of microelectrode arrays using insulated platinum wires of 15 and 25µm diameters. Stable and reproducible performances are achieved from most of the electrodes tested so far (Fig.1). After optimization of the preparation process of the single electrodes they are connected in meshes of 4, which will be later used for analysis in 3D cell cultures.

Simultaneously, we are also working on the development of glucose biosensors as they can be easily modified to sense other species such as glutamate by mere exchange of the enzyme, yet glucose oxidase is much less expensive and easier to work with than other enzymes from the oxidase family. Apart from glucose oxidase the sensor is covered with a layer of a mediator. We are investigating both Prussian Blue (Fig.2) and a metallopolymer that contains poly(vinylimidazole) (PVI) complexed with [osmium-(4,4'- dimethoxy-2,2'-bypyridine)Cl] (Os-dmo-bpy).[3] As the neural cells will be growing directly on the electrodes, we are not neglecting the possibility of accidental stimulations as the neural culture is electrically active and the potential in standard electrochemical measurements is swept till 1.0 V or higher. Although hydrogen peroxide produced through the reaction with oxidase enzyme can be sensed directly on a platinum electrode, we apply a layer of a mediator to reduce the working potential of the electrode and diminish the chance of accidental stimulation of the culture.

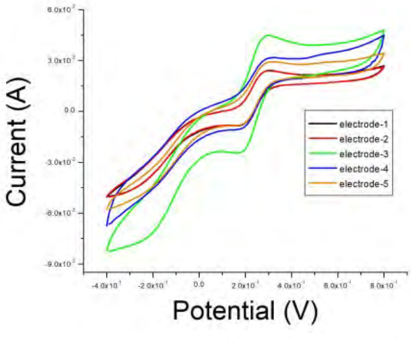

Fig.1 Stable and reproducible performances of five 15 µm platinum microelectrodes in 1mM 1, 1'-Ferrocenedimethanol and 0.1M KCl

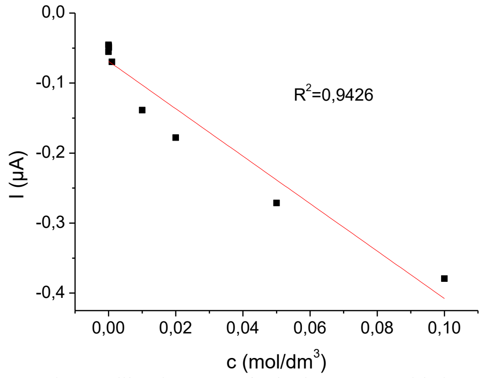

Fig.2 Calibration curve for hydrogen peroxide in PBS Buffer (pH 7.4) measured using Prussian Blue modified glassy carbon electrode vs Ag/AgCl 1M KCl

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Multilayered DDM-modified Nickel foam anodes for alkaline water electrolysis

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Water electrolysis provides a direct pathway for conversion of electrical energy to chemically energy in the form of high-purity hydrogen.

Currently, commercial approach for low temperature water electrolysis is the alkaline water electrolysis (AWE). The alkaline water electrolyzers typically operated in aqueous KOH solutions (c= 25–30 wt% (5.5–6.9 M KOH) and T= 65 °C and 100 °C) where cathode and anode compartments are separated by a porous diaphragm, allowing the conduction of hydroxide ions while separating the product gases.

The AWE offers the distinct advantage of employing relatively inexpensive non-noble electrocatalysts (nickel-based catalysts are most commonly used), which provide for relatively low oxygen evolution reaction (OER) overpotentials and good stability in alkaline media.

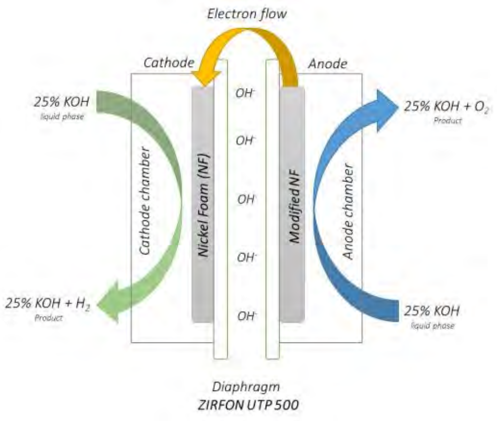

Fig. 1. *AWE setup with immersed porous NF electrodes in zero-gap assembly*

In the present work, a concept for alkaline water electrolyzer with a ‘’Dip and Drying’’modified (DDM) nickel foam (NF) electrodes as anode, a pure NF cathode and a state-of-the-art Zirfon™ separator is presented. The geometric surface of the electrodes was 7 cm^2.

The DDM-NF anode consist 1 mm thick Nickel foam substrate covered with thick micro-pores catalytic layer build from DDM -Nickel powder and PTFE emulsion.

The morphology and the chemical composition of the developed materials/electrodes were analyzed by scanning electron microscopy (SEM) and X-ray difraction (XRD), respectively.

The electrocatalytic activities of the electrodes for the hydrogen (HER) and oxygen (OER) evolution reactions in 1M KOH are investigated by linear sweep voltammetry (LSV), cyclic voltammetry (CV), and chronopotentiometry (CP). Then, the electrodes were fixed in a laboratory made electrolysis test cell and separated by a 0.5 mm thick ceramic diaphragm Zifron Perl 500 (Fig.1). The doping of the diaphragm was performed directly in the cell by circulating 25% KOH solution for 24h at room temperature.

The single cell unit operated in dynamic regime at room and elevated temperatures without any sign of degradation. The current density reached value of 0.150 $A.cm^{-2}$ at 80 ^{0}C and 2V cell voltage.

Acknowledgements: The research has been supported by the National Research Program " Young Scientists and Postdoctoral Fellows "-2020, Bulgarian Ministry of Education and Science.

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Understanding the Effect of Interfacial Interaction on Metal/Metal Oxides Electrocatalysts for Hydrogen Evolution and Hydrogen Oxidation Reactions on the Basis of First-principle Calculations

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Abstract : Understanding the interfacial interaction between metal (M) and transition metal oxides (TMO) support is essential for the material design of high performance electrocatalysts. In this study, we constructed Pt/TiO_2 composite models with interfacial Pt-Ti and Pt-O bonds respectively, to clarify the interface effect on electronic structures, species ad-desorption and migration properties, HER and HOR mechanism through first-principles calculations. Interfacial Pt-Ti metallic interaction causes more delocalized electron on Pt cluster, which strengthens H and OH adsorption, facilitates *H migration and H_2O dissociation. While interfacial Pt-O covalent interaction affects the localized electronic structure of Pt with deficient electron, which results in an optimum H ad-desorption and complicated *H migration processes. The interface sites and non-interface sites jointly provide an efficient H migration channel and reaction pathway. For HER, Pt-O interaction benefits the Tafel step, and Pt-Ti interaction is favorable for the Volmer step. For HOR, Pt-O interaction contributes to a higher HOR activity and an anti-oxidation ability than Pt-Ti. These results can serve as a theoretical guidance for constructing high performance M/TMO electrocatalysts for HER/HOR by regulating interfacial bond type and proportion.

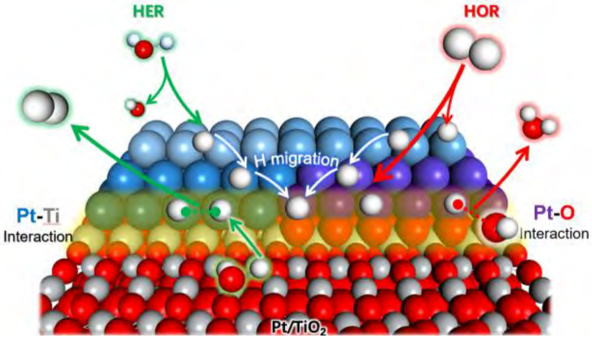

Figure 1 Interfacial Pt-O and Pt-Ti interactions of Pt/Ti contribute two distinct tune effects on HER/HOR.

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The Influence of Flow Field Design on the Performance of a Zinc-Iodide Flow Battery

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A very high energy density has been reported for the zinc-iodide flow battery [1]. An optimized flow field design for uniform distribution of the electrolyte is desirable for the redox flow battery systems. In order to enhance the performance of a zinc-iodide flow battery, the impact of a new flow field design on the performance of the battery was investigated.

The flow cell used graphite felt electrodes, a Nafion membrane, and had an active area of 5 cm^2. Electroanalytical methods, including cyclic voltammetry (CV), and rotating disk electrode (RDE), were performed to evaluate redox potential, diffusion coefficient and electrochemical reversibility of the electrolyte system.

Charge-discharge characteristics were carried out to investigate cyclability and efficiency of the zinc-iodide battery with and without the presence of flow-through flow field design. The battery cell was tested under constant current density over 40 cycles and test analysis indicated that the efficiency and discharge energy density of the battery improved. Using scanning electron microscopy (SEM) and optical profilometry shows that the presence of flow-through flow field design enhanced the morphology of zinc deposition from a thick and rough deposition to a thinner and soft deposition in the new flow field design. It was also found that due to inhibition of dendrite formation with the presence of flow-through arrangement, a higher range of current density is applicable for the zinc-iodide flow battery.

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Electrochemical conversion of carbon dioxide to oxalate and oxalic acid

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The electrochemical CO_2 conversion technology has merits of the operation at room temperature and atmospheric pressure, and the flexible capability in the scale by stacking and attracts a lot of attention from the industries to capture and convert the CO_2 to useful compounds. Oxalic acid is a reduced dimer of CO_2, and it uses only one-electron per CO_2 for the conversion. It can be one of the most economical and energy-efficient CCU (carbon capture and utilization) processes. We succeeded in producing 0.1 kg/day of the oxalate salt at the current efficiency of 86% in the one-pot cell using a sacrificial anode. Subsequently, the oxalate could be converted to oxalic acid with an efficiency of 75%, by the membrane electrolysis using a three-compartment cell.

Nickel Phosphide Coated with Ultra-Thin Nitrogen Doped Carbon Shell as a Highly Durable and Active Catalyst for the Hydrogen Evolution Reaction

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With the aggravating environment pollution and depletion of conventional fossil fuel, the development of clean and sustainable energy, such as solar and wind power, has become a worldwide research hotspot [1]. However, the development of wind and solar energy still face the feasibility problem due to their intermittent nature [2]. Fortunately, water splitting offers an ideal route. Water can be used to store solar and electrical energy to produce hydrogen. This can be realized by electrochemical reactions, which is an efficient method to store electrical energy at scale. Therefore, water electrolysis process plays an important part in the construction of the energy conversion system.

The greatest challenge is the design and fabrication of efficient catalysts for the hydrogen and oxygen evolution reactions of water electrolysis. Although Pt and Pt-based materials are the most effective catalysts for hydrogen evolution reaction (HER) at present, the high cost and low abundance hamper their wider uses. High abundance non-precious catalysts based on transition metals including Ni, Co, Mo, and W are more intensively studied and regarded promising in replacing Pt based materials. Among the varied transition metal based catalysts, transition-metal phosphides, especially nickel and cobalt phosphides, has long been considered as the most effective non-precious electrocatalysts for HER.

To solve the problems mentioned above, herein, highly durable and active Ni_2P nanoparticles with ultrathin N-doped carbon shell are fabricated. With the aim of improving the stability of Ni_2P nanoparticles without affecting their electrocatalytic activity, the number of N-doped carbon layers is controlled. By controlling the thickness, the protective shells are ultrathin (as low as 4 layers) and permeable for the reactant molecules, which avoid catalytic active sites being blocked. In addition, the effect of N dopant on the catalytic activity of the hybrid material is also discussed. As recently published, the sulfur incorporation into transition metal phosphides leads to more optimal ΔG_H* (0.096eV), and achieves the balance of hydrogen adsorption and detachment on Ni sites. Inspired by the similar electronegativities of N and S, herein, N is doped into the carbon matrix to optimize the ΔG_H* of Ni_2P towards better HER activity.

Acknowledgments

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Numerical Modelling of Silicon Electrodeposition ~~by~~ in High Temperature Molten Salt Electrolysis

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Current manufacturing of silicon for solar energy applications via the Siemens process is expensive, energy intensive, unsafe, and environmentally harmful. It involves ~~due to~~ many unit operations, including carbothermic reduction, chlorination, distillation, and vapor phase reactions. Many r~~energy intensive with inefficient carbothermic reduction and has various safety problems. R~~esearchers have considered direct electrolysis of silica employing ~~looked at alternative methods and the electrodeposition of silicon using~~ molten salts ~~is a promising process~~[1]. This process is analogous to aluminum smelting in the Hall-Heroult cell. Towards this goal, a novel molten salt bath comprising of MgF_2-CaF_2-YF_3-CaO-SiO_2 was formulated. It has ~~to have~~ low volatility <0.1 µg/cm^2*s, low viscosity of <5 mPa*s, high ionic conductivity of >4 S/cm and adequate SiO_2 solubility >5wt% [2]. ~~One of t~~The scientific challenges ~~obstacles~~ that remains are ~~to be answered is~~ the salt entrapment and the non-planar and non-uniform growth of the silicon deposit~~the characteristics of the deposition~~. To address these challenges an understanding of the deposition process is necessary. ~~The current density distribution on the electrodes, and the characteristics of the bath gives us an idea of the growth pattern of silicon on the cathode and the losses that can occur in the electrochemical cell.~~ This presentation provides a model of the silicon deposition process ~~looks at answering these questions throug~~through~~h~~ a macroscopic finite element model by numerically solving the Butler-Volmer equation describing charge transfer overpotential vs. current density, Navier-Stokes equations for fluid flow, energy and species diffusion equations with electromigration [3], and Maxwell's equations describing ~~to understand~~ the magnetohydrodynamics of the bath. It presents quantifiable characteristics of the bath behavior which can be used in design and scale-up ~~ing~~ of the cell. The finite element model is solved using COMSOL multiphysics.

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Enhancing Electrode Durability, Process Intensification, and Co-Conversion for Efficient Electroreduction of CO_2

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Today fossil fuels serve as the major feedstock for the production of intermediates, chemicals, and fuels. This approach will not be sustainable for many generations: Accessible fossil fuel reserves are dwindling and the energy-intense thermal / catalytic processes typically employed for chemical production are responsible for a significant fraction of the anthropogenic CO_2 emissions. The use of electrochemical reduction of CO_2 to products such as CO, formic acid, ethylene, and ethanol may be a process that will be key to achieving a more sustainable chemical industry. While techno-economic (TEA) and life-cycle (LCA) analyses of these processes indicates their promise, these also highlight the challenge to compete in terms of cost with present day chemical conversion processes operated at scale [1].

This contribution will elaborate on three approaches to bring electrochemical reduction of CO2 closer to a process that can be implemented at scale, while being economically feasible and (close to) carbon neutral. First, while active and selective catalysts have been developed for products such as CO, formic acid, ethanol, and ethylene, the electrodes that are needed in scalable electrolysis configuration do not exhibit the 1000s of hours of lifetime needed to achieve economic feasibility. This presentation will summarize the range of encountered electrode degradation mechanisms [2], before elaborating on recent work towards (accelerated) durability CO_2 electrolysis testing methods, as well as ways to mitigate electrode degradation.

Second, like many electrocatalytic processes, the electroreduction of CO_2 is highly dependent on the exact operation conditions of the electrolysis process. This presentation will summarize a set of system design rules to enhance CO_2 electrolysis performance (Faradaic efficiency, energy efficiency, conversion efficiency) through fine-tuning of a combination of factors: (i) electrolyte composition and pH; (ii) electrolyte flowrate; (iii) CO_2 feed flowrate; and (iv) catalyst loading.[3] More recently, we have found that the use of mixed electrolytes can be remarkable useful for further process intensification.

Third, upon realizing that 90+% of the total energy required to operate a CO_2 electrolysis cell is consumed at the anode by the energy demanding oxygen evolution reaction, we explored alternative, less energy-demanding options for the anode reaction. We found, for example, that co-conversion of CO_2 (reduction at cathode) with organic waste molecules (oxidation at anode) reduced the overall energy consumption by 40-50%.[4] This presentation will show how this co-conversion process concept can be the starting point for a new generation of chemical manufacturing technology that is significantly more efficient and sustainable (sustainable feedstocks, less greenhouse gas emissions) than the traditional thermochemical processes.

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Development of a tyrosinase biosensor based on a boron-doped diamond electrode for phenol detection in wines.

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Polyphenols are a large group of organic compounds, that can be characterized by the presence of one or more hydroxylated benzene rings in their structure. In wines two main forms of polyphenols are found; Flavonoids (e.g. quercetin) and Phenolic acids (e.g. gallic and caffeic acid). Because of their useful properties (e.g., antioxidant, anti-mutagenic, anti-carcinogenic etc.) some polyphenols such as curcumin or tannic acid are considered useful reagents, in the treatment of cancer and diabetes. However, other polyphenols such as chlorinated (e.g. 2-chlorophenol) and oestrogenic polyphenols (e.g. Bisphenol) present toxicity and bioaccumulation issues even at low concentrations, thus highlighting the need for simple, selective and highly sensitive electrochemical determination of these for wine analysis, effluent remediation and other purposes.

The aim of this project is the development of an electrochemical biosensor, based on a boron-doped diamond electrode (BDDE) for the determination of tannic acid in aqueous media. The tyrosinase (Tyr-ase) modified electrode was investigated, with special emphasis on the determination of tannic acid. Immobilization of the enzyme onto the electrode active surface confirmed that the enzyme retained its bio-electrocatalytic activity for tannic acid oxidation, which was investigated by means of voltammetric techniques. Tannic acid stock solutions of 5ml were prepared daily, and characterized by attenuated total reflection (ATR) and ultra-violet (UV-Vis) spectroscopy to confirm the functional groups and chemical structure of tannic acid.

A 1.03×10^{-8} M enzyme solution was prepared from a 3.71×10^{-5} M stock solution. Electrode cleaning was done using alumina slurries with particles sizes of 0.05um and 0.3um, with polishing pads. Electrodes were also sonicated in ethanol and water for 5 minutes each, before electro-activation in 1.0M H2SO4 for 15 cycles at 50mV/s and in ultra-pure (Milli-Q) water for 10 cycles at 100mV/s respectively. The Tyr-ase/BDDE biosensor was applied for the detection of tannic acid, and the overall activity of the enzyme was investigated with cyclic and square wave voltammetry. These voltammetric techniques yielded a limit of detection of 0.484mg/L and a limit of quantification of 1.466mg/L with concentrations ranging from 0-6.5mg/L for tannic acid. The biosensor system yielded reasonably high sensitivity and stability for the determination of tannic acid with a standard deviation of 3.25 x 10 -3.

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Probing Interphase Reactions on Lithium with *Operando* Gas Chromatography

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Li battery chemistries exploit reactions that occur under very reducing conditions (~ 0 V *vs.* Li/Li$^+$) at negative electrodes, which are held below the electrochemical stability window of known carbonate-based electrolyte systems (0.5-1 V *vs.* Li/Li$^+$),[1] resulting in solvent decomposition at the surface and leading to the formation of a solid electrolyte interphase (SEI). When formed on Li, however, this interphase is unable to fully protect the electrode, resulting in an SEI composition that changes over time.[2] Due to this dynamic nature, its chemistry is challenging to characterize using conventional *ex-situ* surface analysis (*e.g.*, Fourier transform infrared spectroscopy, FTIR; X-ray photoelectron spectroscopy, XPS).[3, 4] Consequently, identifying the chemical mechanisms through which candidate systems for improving Li SEI stability operate – such as the use of highly fluorinated and/or concentrated electrolytes[5] – remains difficult. Fortunately, interphase reactions are known to release gases that are easily detected by gas chromatography (GC) and mass spectrometry (MS),[6] using which we are able to construct a time-resolved picture of the SEI chemistry. Here we show that these experiments can provide valuable insight into the dynamic chemical reaction pathways on Li, yielding an updated picture of factors that contribute to a good SEI.

Our experimental approach consists of a custom-designed electrochemical cell coupled to a GC instrument, which, by sampling the cell headspace periodically, enables *operando* quantification of CO_2, CO, H_2 and C_{1-2} products evolved at Li electrodes. By comparing gas evolution between rest and polarization regimes, we identified a significant increase in the rate of formation of all observed gases when the electrodes are polarized. Using electrodes that we identified to be gas-inert, such as $LiFePO_4$, we identified that the deposition reaction, *i.e.*, Li$^+$ reduction, accounts for nearly all of the gas-releasing interphase reactions, implying that the SEI is only formed electrochemically when Li is plated. We next explored the nature of these reactions by quantifying how the evolution rate of each gas scales with current density, which enabled the distinction between gases that were formed in chemically-limiting reactions and gases that were formed from electrochemically-limiting steps. Because our experiments are able to quantify the abundance of each gas product, we also identified and quantified the branching of specific interphase reactions that occur on Li with conventional carbonate-based electrolyte systems. Then, by rationally tuning the electrolyte (*i.e.,* changing the salt species and/or introducing fluorinated solvents), we discovered and quantified how each component drives specific interphase reactions, and how the ensuing SEI chemistry affects the Faradaic efficiency of the Li electrode over time. In particular, we observed that pathways that promote decarbonylation and/or decarboxylation (*i.e.*, release of CO/CO_2) of the solvent upon reduction correlate with higher Faradaic efficiencies. By varying salt concentration, we further explored how interphase formation pathways are affected by the solvation structure of the electrolyte in the contact-ion and solvent-separated regimes. Thus, our experiments provide a mechanistic picture of how organic solvent-derived products affect SEI chemistry and stability, which can be as important as known ionic phases like LiF.[5]

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Ferrocene Oxidation Study in Water-in-Biodiesel Microemulsions

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New electroanalytical methodologies in low conductivity media such as fatty acids alkyl esters, also known as biodiesel, have been of great interest in analytical chemistry. Self-oxidation of pure biodiesel (B100) gives rise to secondary oxidation products so that B100 oxidative stability is a quality criterion that requires regular monitoring. Therefore, rapid and direct quantification of species present in biodiesel is important to allow adjustments and ensure product quality even in production line. A study on oxidation of ferrocene (Fc) in aqueous media by Bond et al (1) showed poor adsorption on the electrode surface so that, even so, the Fc^+/Fc redox pair can be used as a reference system in this medium. In the present study, B100 samples prepared in water in oil microemulsion (w/o ME), containing ferrocene (Fc) as a probe were analyzed using differential pulse voltammetry (DPV) at a Pt ultramicroelectrode (ume), to evaluate oxygen influence in this medium. A µAUTOLAB TYPE III potentiostat/galvanostat provided with a general-purpose electrochemical system (GPES) software has been used in voltammetric measurements conducted in a three-electrode configuration cell. The working electrode was a 10 µm radius Pt disk ume, while a Pt ribbon and a Pt wire were, respectively, the auxiliary and quasi reference electrodes. Successive additions of Fc in w/o ME were made in concentrations ranging from, respectively, 1.2×10^{-3} mol L^{-1} to 2.1×10^{-3} mol L^{-1}. Experimental conditions were: 10 mV amplitude; 50 ms pulse width and 5 mV s^{-1} potential scan rate. All voltammetric measurements were carried out at room temperature without stirring. Influence of oxygen was evaluated de-aerating the system through bubbling nitrogen for 5 minutes. The B100 sample was used within specifications set by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP). The ME was prepared in % mass/mass with water (9%), B100 (28%) and sodium dodecyl sulphate (SDS):n-pentanol (1:4) (63%). Microemulsion components were mixed sequentially and mechanically stirred until obtaining a clear and homogeneous system. It was observed that a current peak, i_p, which doubles in value with increasing concentration of Fc appears at a potential, E_p, around 0.100 V. In the same scan, around 1.400 V there is a second current peak which also increases with Fc concentration. However, when the system is de-aerated, the first peak remains unchanged whereas the second one practically disappears. This behavior may be indicating that there is a chemical reaction between oxygen and Fc or Fc and some ME component. The first peak could also correspond to oxidation of Fc dissolved in the continuous medium, which requires less positive potentials, while the second one would correspond to ferrocene dissolved into the water droplets. In this hypothesis, the droplets surfactant-cosurfactant envelope would require a more positive potential for its rupture to release dissolved Fc. The results obtained for the redox reaction of the Fc^+/Fc pair in the studied system show a good relationship between Fc concentration and the measured current, as well as influence of oxygen in the medium, as already described for polar organic solvents (2). Thus, it has been demonstrated that preparation of B100 samples as w/o microemulsion enable analysis by differential pulse voltammetry, de-aeration of the medium being recommended.

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Simulation of an Interdigitated Monopolar plate for a Cation Exchange Membrane Fuel Cell

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The increasing energy demand, finite nature of fossil fuel resources and global environmental challenges have promoted the development of alternative energies and green technologies. Proton exchange membrane fuel cells (PEMFCs) are promising alternatives because they convert chemical energy from hydrogen and oxygen (or air) into electricity with high efficiency, high power density, and low or zero pollutant emissions[1]. Several studies have been done to improve the overall efficiency of PEM cell stacks including the development and selection of an adequate catalyst layer, proton exchange membrane, gas diffusion layers and flow channels configurations. Bipolar plates (BP) are one of the most important components in cell stacks because they perform several functions like supply the reactant gases through the flow channels, provide structural support and facilitate water and heat management [2]. Inadequate design of BP leads to bumpy reactant gases distribution, localized hot spots, uneven current density and flooding of the device caused by poor water management [3]. Numerous studies have been done to improve the bipolar plate design, in this context, interdigitated flow fields rise to prevent water flooding phenomenon and promote a better mass transfer through porous media [4]. Biomimetic flow fields, inspired on nature, have been designed to reduce the pressure drop and current distribution, and water removal. In the present work, computational fluid dynamics (CFD) simulations of an interdigitated flow field based on leaf veins was carry out to be tested on a cathodic compartment in PEMFC.

Model development for CFD simulations is based on the Navier-Stokes equations coupled to continuity equation for a free flow through channels and Brinkman equations on porous media; governing equations for mass transfer are described by the Mixture-averaged transport model with the Bruggeman´s correction for porous media and the electrochemical kinetic is represented by the Butler-Volmer equation. The transport equations were solved numerically in 3D by finite element method using the software COMSOL Multiphysics. CFD simulations were carried out in order to analyze the effect of different operation variables on cell performance. Finally, simulation results were validated using experimental. A computer numerical control (CNC) machine with one-way trajectory was used to produce the interdigitated monopolar plate to carry out cathodic experiments with the aim of validating the CDF simulations.

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Fabrication of the Electrochemical Cilostazol Chemosensor with Molecularly Imprinted Polymer Nanoparticles as the Recognition Unit

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In the presented paper, fabrication, and tests of an electrochemical chemosensor for selective determination and quantification of cilostazol is described. Cilostazol, 6-[4-(1-cyclohexyl-1H-tetrazol-5-yl)butoxy]-3,4-dihydro-2(1H)-quinolinone, is an antiplatelet agent and a phosphodiesterase III inhibitor. It is used for the treatment of intermittent claudication (IC), a preliminary symptom of peripheral arterial disease (PAD). PAD is most commonly caused by atherosclerosis. It affects millions of patients worldwide and is associated with significant morbidity and mortality.[1] Fast, simple and reliable method of this drug determination along with its principal active metabolites is important from the point of view of personalized drug dosage. In order to devise selective chemosensor for determination of cilostazol in biological matrices, molecularly imprinted polymer nanoparticles (nanoMIPs) were prepared by precipitation polymerization of the selected acrylate derivatives and were characterized.[2] Furthermore, density functional theory (DFT) calculations were performed for better understanding of interactions between the acylate monomers and the target analyte, and also with its principal metabolites. The result indicated pre-polymerization complex formation mainly through H-bonding.

In the next step the nanoMIPs were immobilized on the gold electrode. Then, the obtained electrodes were characterized electrochemically and spectrally. Moreover, morphology of the obtained electrodes was studied by AFM microscopy. Finally, the analytical tests of the devised chemosensor were performed.

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Mn_2O_3-based catalysts for regenerative fuel cell applications

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Rising global warming by CO_2 emissions from fossil fuel combustion and increasing energy demands have led researchers all over the world to focus on developing technologies for clean energy production. Fuel cells and batteries are in the focus of many research groups and have great potential to replace fossil fuel-based technologies for numerous applications. In order for fuel cells to produce high currents, high performing metal-based catalysts for oxygen reduction reaction (ORR), oxygen evolution reaction (OER), hydrogen oxidation reaction (HOR), and hydrogen evolution reaction (HER) are of great importance. In this work, we synthesized manganese oxide-based catalysts as cathode materials for regenerative fuel cell applications. Three catalysts based on Mn_2O_3 were synthesized: Mn_2O_3 in pure form, Mn_2O_3 with anchored Pt nanoparticles (NPs), and Mn_2O_3 with Pt and Ni NPs. Ni and Pt NPs were anchored via microwave irradiation method.[1]

Linear scan voltammetry (LSV) experiments in 0.1 M KOH in ORR potential region clearly show that attaching NPs on pure Mn_2O_3 has a positive effect on limiting current density and onset potential values. For Mn_2O_3 we found limiting current density of -2.31 mA cm^{-2}, while the Pt/Mn_2O_3 sample has shown limiting diffusion current density of -4.00 mA cm^{-2}. PtNi/Mn_2O_3 sample showed a slightly reduced value of limiting current density (-3.17 mA cm^{-2}), but this sample contained only 10 wt.% of Pt and 10 wt.% of Ni NPs, comparing to Pt/Mn_2O_3, which had 20 wt. % of Pt NPs. Pt is well known for its electrocatalytic performance, but also for its high price.[2] LSV experiments performed in the potential region corresponding to OER revealed that all samples exhibit similar behavior in terms of the onset potential of the investigated reaction. After performing IR correction all three LSVs overlapped almost perfectly. The difference could only be observed in maximum current densities that have been reached in each experiment. The highest one is reached with the pure Mn_2O_3 sample, followed by PtNi/Mn_2O_3 sample. The lowest value was shown by the sample containing only Pt NPs. Tested samples showed promising results for both investigated reactions. Having in mind the cost of Pt and comparing its performance with the sample that also contains Ni NPs, we must emphasize the potential of PtNi/Mn_2O_3 catalyst for regenerative fuel cell application. Further analysis should be performed to get better insights into the kinetics of both reactions on these catalysts. Also, one of the main aims of future investigation is testing the stability and their performances in a real regenerative fuel cell.

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Enhanced Photoelectrocatalytic Degradation of Organic Pollutant by Self-organized Nanotubes Grown on Ti14wt.%Nb Substrate Under Different Preparation Methods

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Titanium-based materials have been extensively studied in a variety of different applications. Among them are studies aimed at the photodegradation of pollutants present in water and wastewater, such as dyes. About 10-15 % of the amount of dye produced in the world is released from the process into the environment, which is an alarming issue from an environmental point of view [1]. Thus, different studies have been carried out in order to promote the total mineralization of pollutants into innocuous compounds, such as CO_2 and H_2O. Due to the limitations of the TiO_2 semiconductor (high recombination rate of photogenerated charges; band gap energy 3.2 eV, anatase phase), modifications by decoration or doping with metals or metal oxides have been evaluated as an alternative to improve this semiconductor [2]. Considering that Brazil has the largest reserve of Nb in the world, holding 98 % of the world's reserves of ore, and its low cost, combined with the advantages related to the structural modification by doping and surface modification, this study proposes the production of photocatalytic oxides nanoscale in Ti14Nb alloy. In the niobium-oxygen system the phases NbO, NbO_2 and Nb_2O_5 are the main ones observed [3]. In general, materials which are modified with Nb shows Nb_2O_5 in the composition of the nanotubes (NT), as well as absorption in the visible region due to doping in the oxide matrix. In this context, this work presents the formation of nanotubular oxide layer (NOL) grown on Ti14wt.%Nb substrate under different preparation methods, cast (BF) and quenching (CT). The influence of substrate type, the temperature on the crystallization of oxides and on the performance of the semiconductor photocatalytic activity used in the degradation of Reactive Blue 4 (RB4) dye was evaluated. The nanotubes were grown on Ti14wt.%Nb substrate by anodization process, using HF solution (0.3%, v/v) under a constant potential of 20 V, reached after a voltage ramp of 2 V min^{-1}. Then, the samples were heat treated at different temperatures from 450 to 650 ° C, in order to optimize the conversion temperature of the amorphous structures, resulting from the anodization process, into highly ordered crystalline structures. The oxide layer grown on Ti14wt.%Nb substrate was characterized by SEM, EDX and XRD. Photoactivity studies were carried out and compared among different heat treatment temperatures using the linear voltammetry technique in 0.1 M Na_2SO_4 solution, pH 3, with potential range from -0,025 to 1,5 V *vs*. Ag/AgCl/Cl^- (3 mol L^{-1}). The evaluation of the performance of the alloy in color removal and degradation of the Reactive Blue 4 (RB4) dye by photocatalytic and photoelectrocatalytic processes under UV/visible and visible light was carried out and compared with the TiO_2 semiconductor. The results demonstrated that the addition of Nb in the oxide layer leads to an increase in the anatase-rutile transition temperature. The presence of Nb_2O_5 was confirmed by XRD and EDX analyzes, which give the material a hybrid behavior (partially doped with Nb), even in small quantities. The sample NT/Ti14wt.%Nb-Q showed better photoactivity compared to the sample NT/Ti14wt.%Nb-C and NT/TiO_2. The best condition obtained for the NT/Ti14wt.%Nb-Q sample was under heat treatment at 650 °C, which presented a current intensity of 1.08 and 0.71 mA cm^{-2} under UV/visible and visible light, respectively. Comparing the electrodes studied, in photoelectrocatalysis (PEC) under UV/visible light, NT/Ti14wt.%Nb-Q was more efficient in the degradation of Reactive Blue 4 (RB4), reaching 66 % reduction of the initial carbon concentration [Co] over 1.5 hours, total discoloration after 20 min and total mineralization after 2 hours; while the sample of NT/Ti14wt.% Nb-C reduced 88 % of [Co] in 3 hours and total discoloration after 30 min. The decolorization data for PEC under UV/visible light were adjusted in the pseudo-first order and a constant rate (*k*) of 0.17 and 0.19 min^{-1} was found for the NT/Ti14wt.%Nb-C and NT/Ti14wt.%Nb-Q, respectively, whose value is almost double the value of the obtained for NT/TiO_2 electrode under the same conditions. The better performance of the NT/Ti14wt.%Nb electrode in photoelectrocatalysis was attributed to the doping of TiO_2 with Nb.

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Electrochemical Technologies for Detecting and Degrading Paracetamol

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In this work, the detection and quantification of paracetamol was performed by differential pulse voltammetry (DPV) with a cork-modified graphite electrode. The calibration curve and the limits of detection and quantification for paracetamol were estimated. DPV was compared to high-performance liquid chromatography (HPLC) analysis, leading to a satisfactory result in terms of stability and sensitive response. As a novel aim, a combined electrochemical method for environmental application has been developed to oxidize and detect paracetamol using diamond films and cork-modified graphite electrodes. A set of galvanostatic electrochemical oxidation experiments with 1L of Paracetamol solution were accomplished in order to understand the effect of current density, the concentration of the pollutant and the concentration of electrolyte. Applying DPV in an acidic medium with the cork-modified graphite electrode, it was possible determine the concentrations of PAR (ranging from 0 to 1000 µM), with limits of detection of 8.36µM. The optimal operating conditions were achieved at 60 mA cm^{-2}, 100 mg L^{-1} of Paracetamol with 50 mM Na2SO4. Additionally, the evolution of short-chain carboxylic acids of that test was followed over time in order to suggest a possible degradation route. The results were described and discussed in the light of the existing literature.

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One-step preparation of the Co2V2O7: synthesis and use to peroxide electrogeneration

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Gas diffusion electrodes (GDE) produced with carbon matrices have been applied in the hydrogen peroxide electrogeneration and used in electro-Fenton process. In GDE, an increase of peroxide electrogeneration can be achieved by improving the carbon matrix (CM) or by incorporating electrocatalysts in CM. Different CM has been studied, among them, Printex 6L Carbon (P6LC) has a good cost and efficiency ratio, as it has a high surface area and a selectivity for the oxygen reduction reaction (ORR) via 2 electrons. Regarding the new electrocatalysts studied, bimetallic oxides are being applied as electrocatalysts to ORR, due to the synergism between metals as catalysts for ORR. In this study, a new one-step route to obtain $Co_2V_2O_7$ is described, as well as the incorporation in P6LC that is used in the electrochemical study of ORR, and the application of the modified matrix in the GDE. The $Co_2V_2O_7$ was obtained by co-precipitation from the neutralization of solutions containing the precursors. For this, two solutions were prepared (20 mL): A) 0.1 M HNO_3 + 0.2 M $Co(NO_3)_2$ and B) 0.1 M NH_4OH + 0.2 M NH_4VO_3. Both solutions were heated to 80º C. Then, solution A was transferred drop by drop to solution B, under agitation. After all, the material was filtered, washed with deionized water, and dried at 120º C. The material was characterized by XRD. Diffractogram analysis indicates the presence of the monoclinic phase associated with $Co_2V_2O_7$ (ICSD 2357). Any secondary phases were not observed, and thermal treatment was not necessary, unlike the syntheses reported in the literature. The $Co_2V_2O_7$ oxide was added to P6LC by physical adsorption in the proportions of 2.5, 5.0, 10.0, and 15.0 % (w/w). For this, both catalytic masses were mixed with isopropyl alcohol under magnetic stirring for 40 min, dried for 3 h (2 h at 60 ºC and 1h at 100 ºC). Electrochemical measurements (electrochemical impedance and analysis of the ORR efficiency studies) were performed using the porous microlayer technique applied on the glassy carbon disc. The study of ORR was carried out using linear scanning voltammetry coupled to a rotating ring disk electrode (RRDE) system, with a rotation speed of 100 to 2500 rpm. The PL6C presented a maximum current value of 135 µA. The 15% $Co_2V_2O_7$/PL6C had the highest recorded value, 160 µA, followed by the 2.5% $Co_2V_2O_7$/PL6C with 147 µA, a value close to the 5% $Co_2V_2O_7$/PL6C (143 µA). The modification with $Co_2V_2O_7$ tends to improve CM's selectivity, leading to a higher electrogeneration of H_2O_2. Also, the ORR onset is the same for all catalysts, having a value close to -0.15 V vs. Ag/AgCl, which suggests that the modification does not alter the start of the reaction, only increases its selectivity. However, at low potentials of -0.3 V, a displacement of the current recorded on the disk to more negative values are observed. This shift towards that more negative potentials results in greater consumption of electrical energy from the ORR for the H_2O_2 electrogeneration. The PL6C had shown a value of H_2O_2 selectivity (%) equal to 85.0 %. In the modified matrices the values was: 92.0; 91.0; 90.9 and 86.8% to 2.5; 5; 10 and 15%, respectively. With these results and EIS analysis, the modified matrix with 2.5% $Co_2V_2O_7$ was chosen for the production of GDE. The GDE containing 40% PTFE was prepared by mixing the catalytic mass with the PTFE, in 400 ml of ultrapure water under constant agitation for 60 min. The suspension was filtered, and 2 g of the new mixture was placed between two metal plates under 7.5 tons, 290 ºC for 2 h. Then, the study of H_2O_2 electrogeneration was carried out by electrolysis at constant current density (25, 50, 75, and 100 mA cm^{-2}), using GDE (unmodified, only PL6C) and GDEm (PL6C modified with 2.5% $Co_2V_2O_7$). The maximum concentration of H_2O_2 obtained for the GDE was 132 mg L^{-1}, after 90 min at a current density of -100 mA cm^{-2}. For GDEm, an increase of 33.3% in H_2O_2 electrogeneration was observed (176 mg L^{-1}), for the same current density. Analyzing the energy consumption (EC) for GDEm, the value was 86.2 kWh kg^{-1} to $j = -100$ mA cm^{-2}, lower than observed for GDE (116.3 kWh kg^{-1}). However, the density that showed the best ratio between EC and H_2O_2 electrogeneration was -75 mA cm^{-2}, which produced 147 mg L^{-1} of H_2O_2, and EC was 59.4 kWh kg^{-1}. In conclusion, the proposed new one-route was a simple method to produce a new selective material to H_2O_2 electrogeneration. This material can be adsorbed onto CM to increase the performance of GDEs and to decrease the energetic consumption of these electrodes.

On the electrolysis of liquefied lignocellulosic biomass

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This work aims at producing electrolytic H_2 and explore the possibility of capturing CO_2 through the electrolysis of liquefied biomass. Lignocellulosic biomass is constituted by three main polymers: cellulose, hemicellulose, and lignin [1]. Biomass is globally used for different energy needs including, electricity generation, heat for domestic and industrial use, and transportation fuels. However, biomass is mostly used through direct combustion [2]. The major obstacle for the utilization of lignocellulosic biomass is the cost-benefit relation of used technologies to process this kind of material and produce fuels and high-added value chemical compounds [1]. The electrolysis process of liquefied biomass powered by renewable energy and, consequently, without CO_2 emissions, has the potential for H_2 production (chemical energy storage) scale-up. Furthermore, the electroreduction of CO_2 is a promising approach for the reduction of CO_2 emissions that is receiving increasing interest from the scientific community, policy makers and the general public [3].

For this purpose, voltammetric, chronoamperometric, rotating disk electrode (RDE), and rotating ring disk electrode (RRDE) studies are employed for the electrochemical characterization of an emulsion constituted by a 1:1 mix of liquefied biomass and a 2 M KOH aqueous solution (for the ionic conductivity enhancement). A small-scale laboratory liquefied biomass electrolyzer is assembled and used to analyze the electrolysis optimal working conditions. Temperature, voltage, and different anode materials (Ni and TiO_2-RuO_2) are studied. In all experiments, gas generation is observed at the Ni cathode side. The results show that when Ni electrodes are used for both cathode and anode the generated current is four times higher than employing a TiO_2-RuO_2 anode. Additionally, the use of higher temperatures (55 ºC) generates two times higher currents than those obtained at room temperature. As, expected, currents were also improved when increasing the potential up to 2.4 V. Additional experiments involved CO_2 continuous bubbling in the solution during the electrolysis. The results show that the CO_2 bubbling is able to hold stable the liquefied biomass emulsion's ionic conductivity for significantly longer times than in the experiments without CO_2 addition.

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Computational Core Level Electron Spectroscopy of Ionic Liquids in Bulk and at Interfaces

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On the example of 40 ion pairs (5 cations times 8 anions), this study demonstrates how the core-level binding energy values can be calculated and used to plot theoretical spectra at low computational cost using density functional theory methods [1]. Three approaches for obtaining the binding energy values are based on delta Kohn–Sham (ΔKS) calculations, 1s KS orbital energies, and atomic charges. The ΔKS results show reasonable agreement with the available experimental X-ray photoelectron data [2–6]. The 1s KS orbital energies correlate well with the ΔKS results. Atomic charge correlation with ΔKS is improved by accounting for the charges of neighboring atoms. The choice between the methods implies a compromise between computational cost and accuracy. For instance, differently from the other methods, the order of ΔKS binding energies is in agreement with the difference spectroscopy used to resolve the order of peaks in pyridinium- and imidazolium-based ILs by comparing the XPS of functionalized and non-functionalized cations [7]. Besides being more accurate, the ΔKS method is also more resource-demanding and less accessible than the other two methods. Thus, the use of the 1s KS orbital energies and atomic charges is justified when qualitative aspects of X-ray photoelectron spectra are of higher interest than the absolute BE values, or when the available computational power is limited. For example, the experimental data taken from [2–4] measured in connection to the electrochemical application in the supercapacitors. On example of graphene–ionic liquid interface, we show that 1s KS orbital energies and atomic charges can be obtained in molecular-level simulations of a supercapacitor model at a relatively low cost.

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3D topographical SVET prototype for localized corrosion study.

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The Scanning Vibrating Electrode Technique has been applied to corrosion research for few decades and proved its relevance especially in specific localized corrosion research on carefully designed model-electrode situations. However, due to the technical restrictions several limitations to the sample conditions have to be taken into account, especially the sample size and topography, as the ionic currents under observation are rapidly dependent on the probe to surface distance.

New technical approach of combining the scanning confocal microscopy and 3D resolved SVET will be presented. Several topographically complicated and demanding model electrode systems were explored and the approach of localized electrochemical technics will be discussed and evaluated.

The Different Al alloys (such as aeronautically relevant AA2024 and modern Al-Li alloy AA2198) are given as studied examples for estimation of corrosion localization and it's influence. Also, the different technologically relevant galvanic situations like CFRP + Al alloys or Ti + Al are considered in respect of design of dedicated corrosion inhibiting systems and its relevance of application of new approaches of SVET technique.

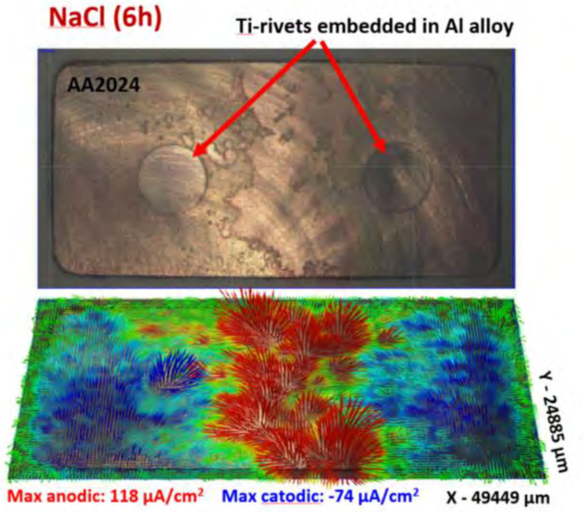

Figure 1. Photograph and 3D SVET map of AA2024 sample with two embedded Ti rivets immersed in 0.05M NaCl for 6h. Localized distribution of galvanic corrosion activities are exposed.

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Smart Electrochromic Devices based on Luminescent Ionosilica/Poly(methyl methacrylate) Electrolytes

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The pressing energy challenges for the coming years call for new materials and new technologies. In the building sector, the need to increase the buildings energy-efficiency must be urgently addressed. The use of low-carbon technologies and renewable sources is essential to implement zero-energy buildings (ZEBs). For instance, efforts to considerably improve the performance of the current photovoltaic (PV) cells and to integrate them into buildings must be made. Luminescent down-shifting (LDS) layers and luminescent solar concentrators (LSCs) are valuable options to tackle this issue. LDS layers are coatings directly applied on the PV cell surface, which absorb the incident radiation complementary to that of the PV cell, and subsequently re-emit it at a specific wavelength that is refracted towards the PV cell. LSCs can be embedded in façades or windows, allowing them to be transformed into energy harvesting units, operating similarly under direct and diffuse sunlight conditions. Another attractive way of increasing energy efficiency in buildings is to incorporate smart electrochromic devices (ECDs) able to modulate sunlight transmittance (visible radiation) and solar heat gain (near-infrared (NIR) radiation) and thus reduce the buildings energy use, increase indoors thermal/visual comfort, and improve outdoors view.

Trivalent lanthanide (Ln^{3+})-based complexes exhibit attractive photoluminescence features, but display poor mechanical properties and low thermal stability. To circumvent these disadvantages these compounds may be added as complex anions of ionic liquids (ILs) whose cations are covalently bonded to the surface of silica to yield luminescent ionosilicas (ISs) [1]. In the light of this approach, we produced optically active coatings for LSCs composed of poly(methyl methacrylate) (PMMA) and imidazolium-based ISs containing Eu^{3+}- and Tb^{3+}-based complex counter anions [2]. Recently IS-PMMA LDS layers were coated on the surface of commercial Si-based PV cells. By controlling the down-shifting layer thickness, the layers also acted as LSCs enabling the collection of the guided radiation by flexible PV cells applied on the borders of the down-shifting layer leading to a marked enhancement of the PV energy conversion. Herein, the electro-optical performance of luminescent ECDs incorporating electrolytes composed of a mixture of Eu^{3+}-doped IS-PMMA and an IL, was tested.

Acknowledgment

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Rotating disk electrode studies on the oxidation of kraft black liquor

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The mechanism of the electrochemical oxidation of kraft black liquor (BL) is extremely complex and, to further understand it, a combination of different techniques is required. Simple voltammetric studies, chronoamperometry, and chronopotentiometry have been employed in the electrochemical characterization of BL [1-4], but the results do not provide enough information to elaborate an oxidation mechanism. To collect more data about this process and help in the construction of a logical mechanism, further studies employing rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) are required.

This study deals with the analysis of the effect of the convection (rotation) in the BL oxidation employing commercial bulk Pt, Au, and Ag RDEs. The effect of temperature under convection is also analyzed and compared with the same effect in diffusion-limited conditions. The number of exchanged electrons is calculated by applying the Koutecky-Levich method and compared with the results obtained by Randles–Sevcik equation (in the absence of convection). The electrochemical behavior of black liquor at the three different electrodes is compared to understand how the electrode material affects the mechanism of the BL oxidation. To the best of our knowledge, this is the first black liquor RDE study to be reported.

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Voltammetric and degradation studies of raw and anaerobically digested swine wastewater

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Swine wastewater (SW) is a complex wastewater composed of organic and inorganic contaminants. These substances mainly include polysaccharides, proteins, lignin, and short-chain fatty acids, but also pathogens, antibiotics, trace metals (e.g., Zn, Cu), and salts (e.g., NaCl, KCl) [1]. Electrochemical methods have been widely used for the mineralization of a wide range of environmental pollutants from wastewaters containing varying amounts of inorganic ions and organic compounds with a growing interest in SW as a target solution [2].

However, little is known about the fundamental mechanisms that rule the oxidation of pollutants in these wastewaters. In fact, fundamental electrochemical studies dedicated to understanding the electrochemical behavior of these wastewaters as a background electrolyte are very limited. This knowledge is important because low-grade electrolytes can be used in alternative strategies for hydrogen production from water by replacing the challenging oxygen evolution reaction with thermodynamically more favorable organic oxidation reactions that occur at a lower redox potential [3,4].

Based on these premises, this work aims to present voltammetric studies to obtain a better knowledge of the anodic processes (organics oxidation) occurring during the electrolysis of swine-derived solutions. In particular, cyclic voltammetry using a Pt electrode was used to get a preliminary portrait of the electrochemical behavior of two swine solutions: raw wastewater (RW), as collected from a pig farm, and digested wastewater (DW), as the effluent from the anaerobic digestion of the same wastewater. Subsequently, to analyze possible oxidation processes, voltammograms were recorded at different scan rates (5 - 1000 mV s^{-1}) and conclusions were drawn about the nature of the electrochemical process. The electrochemical degradation of raw and anaerobically digested SW samples was also investigated over graphite and nickel electrodes in potentiostatic conditions. The obtained results suggest the development of the concept of a SW electrolyzer that can be installed in future pig farms.

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Kinetic Study of the Oxygen Reduction Reaction on Conductive Polymer Electrodes Decorated with ZIF-8 as an O_2 Pre-concentrator

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The oxygen reduction reaction (ORR) is one of the most studied in electrochemistry due to its participation in energy conversion devices. Its slow kinetics leads to the inevitable use of catalysts. Within this context, considerable attention was dedicated to electrocatalysis at conducting polymers (CPs) electrodes, its high conductivity and chemical stability makes them very suitable for electrocatalysis purposes [1]. An example of them is CP poly(3-aminobenzylamine-co-aniline) (PABA), copolymer of aniline (ANI), an ORR catalyst, and 3-aminobenzylamine (ABA), which allows the catalysis to occur at neutral pH. One way for increasing the efficiency of these catalysts is the pre-concentration of the O_2 reagent on the surface of the electrode. To achieve that, organometallic networks (MOF) are used as a novel three-dimensional microporous architecture. In particular, the MOF ZIF-8 (Zeolitic Imidazolate Frame), obtained via the polymeric reaction between $Zn(NO_3).6H_2O$ and 2-methyl-imidazole, is widely employed as an O_2 preconcentrator at the electrocatalytic interface.

On the other hand, aniline polymer (PANI) is known to reduce O_2 through the formation of H_2O_2 in a two-electron process [2] but nothing is specifically known about the O_2 reduction mechanism in PABA. Meanwhile, the path of the O_2 molecule through the pores of the ZIF-8 is more turbulent than in solution, being able to modify the kinetics of the conductive polymer.

In this work we will present the development of an electrode composed of the PABA film decorated with ZIF-8 crystals and results from rotating disk electrode (RDE) experiments, performed in order to model the kinetics of the system.

First of all, we will show the electropolymerization of the catalytic copolymer PABA. The obtained nanofilm has been characterized electrochemically and studied by atomic force microscopy (AFM), making possible the elucidation of the surface topography and the determination of its thickness. We will also present the characterization of the ZIF-8 crystals grown onto the PABA-coated electrode, which consist of scanning electron microscopy (SEM) and AFM studies, with the purpose of obtaining details of its microstructure, and X-ray diffraction (XRD) to describe its crystalline nature. Additionally, we will show an ORR linear scan voltammetry (LCV) of the system carried out to demonstrate the effective improvement provided by the ZIF-8 crystals in the catalytic activity of the PABA copolymer for the ORR. Finally, we will provide RDE results that will make possible to establish the kinetic mechanism of the ORR catalysis by PABA and whether or not such mechanism is altered by the presence of the ZIF-8 crystals.

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Electrochemical investigation of heat treated PtRu nanoparticles prepared by modified polyol method at varying pH for direct methanol fuel cell application.

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This study investigated the binary PtRu electrocatalyst prepared by modified polyol method for methanol oxidation reaction (MOR)in acidic medium for the synthesized Platinum- Ruthenium metal alloys supported on multi-walled carbon nanotubes (MWCNT) . HR-TEM and XRD techniques were used to determine the particle size and crystalline size of the electrocatalysts, respectively while EDS was used to determine elemental composition. XRD crystalline sizes are from 7.6 to 10.6 nm while from HR-TEM particle sizes are in the range of 9.3 and 11.3 nm. The electroactivity towards the kinetics and stability of the electrocatalysts towards methanol in acidic medium was studied using electrochemical impedance spectrometry (EIS) and chronoamperometry (CA) respectively, while the cyclic voltammetry (CV) was used to determine the electroactive surface area (ECSA) of the electrocatalysts. PtRu electrocatalysts produced by the modified polyol method at pH 11 were the most electrochemically active with value of $11.2X10^5 g/m^2$ compared with a value of $3.2X10^5 g/m^2$ at pH of 3 Electrocatalysts produced at 450^0C showed better activity towards methanol oxidation reaction(MOR)as compared to PtRu nanoparticles produced at 350^OC and 250^OC evident from the highest current density produced. PtRu nanoparticles produced at 350^0C also gave a remarkable kinetics from the electrochemical impedance spectroscopy but at 450°C the electrocatalyst showed best kinetics for the methanol oxidation reaction.

Keywords: Methanol oxidation reaction, electrocatalysts, multi-walled carbon nanotubes, metal alloys

Electrocatalysis Assisted by Unique Atoms Deposited on Single Crystal <001> Magnetite Surfaces

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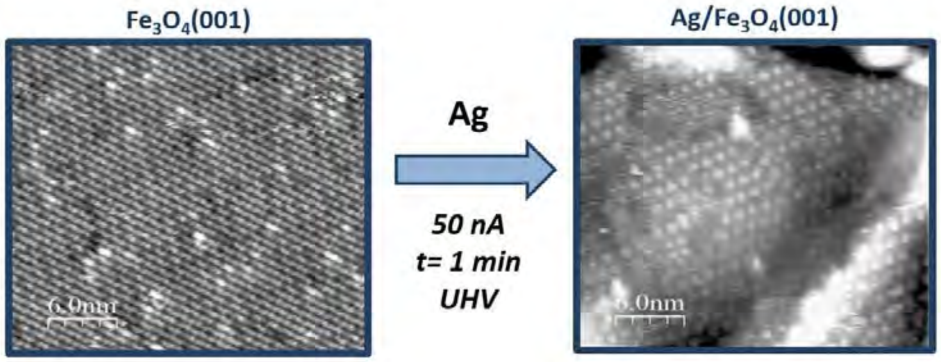
The oxygen evolution reaction (OER) is of great importance in electrochemistry due to its participation in clean energy generation technologies. The main problem with this reaction is its slow kinetics, which leads to the inevitable use of catalysts. The preferred catalysts for this reaction are noble metals, such as Pt or Ag, which have a high cost in the market that is transferred to the technological applications. However, latest efforts are progressively reducing the economic gap with respect to conventional energies, with the single atom catalysis (SAC) as the final limit in minimizing the amount of atoms required to prepare catalysts [1]. Single metal atoms are the best known electrocatalysts for the OER. Nevertheless, their excellent catalytic properties come along with a very high reactivity, making them prone to agglomeration into larger structures with less catalytic power, which in turn impedes the generation of homogeneous coating of individual atoms. To prevent this issue, we propose the use of single crystal surfaces of magnetite (Fe_3O_4) with <001> orientation to act as templates for individual metal atoms. These single crystal <001> Fe_3O_4 surfaces, prepared in ultra high vacuum (UHV) conditions, present a surface reconstruction with nanometric cavities that can act as location sites for individual metal atoms [2]. Recent experiments in our laboratory demonstrated the electrochemical stability of this reconstruction in the range of potentials where the OER occurs [3].



In this work, the adequate preparation of <001> Fe_3O_4 surfaces (under UHV conditions) will be presented, along with first results in the immobilization of individual Pt and Ag atoms; characterization results from scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) techniques will also be available. Furthermore, we will present the electrochemical response of the system to show the catalytic improvement of the OER.

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Effect of the organic solvent on redox rate constant studied by electrochemical impedance spectroscopy

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The presented work is dedicated to study of the solvent influence on kinetics of electrochemical reactions. A great impact within the area was made by W.R. Fawcett et al. [1-2]. A theory relating solvent dielectric properties, longintudinal relaxation time and charge transfer rate constant was successfully used by them to predict electrochemical rate constant based on solvent physical properties. The existent theory, though seemed to be advanced for the time, had revealed numerous limitations that subsequently suspended its wide application. One of the gravest limitations is concerned with the case when electrolyte specifically adsorbs on electrode surface.

Chloranil (tetrachloro-1,4-benzoquinone) reversible one-electron reduction was chosen as a test reaction to study effect of the solvent. The electrochemical process was investigated in seven solvents, including dichloromethane, acetonitrile, toluene, N,N-dimethylformamide, propylene-carbonate, dimethyl sulfoxide, tetrahydrofurane and N-methyl-2-pyrrolidone. The experiment was carried out using platinum working electrode and Bu_4NBF_4 as an electrolyte. A set of impedance spectra were obtained and analyzed by deriving an equivalent electrical circuit and determination of its parameters. Charge transfer resistance, double layer capacitance and other parameters were calculated and represented as a function of potential. Combined analysis of charge transfer resistance and diffusion impedance values allowed estimation of the rate constant for chloranil reduction on Pt electrode. The direct application of the known theoretical approach [1-2] was not possible, probably due to inaccuracies in work-term corrections. The challenges and the proposed solutions are to be discussed.

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Study of Microstructure and Corrosion Properties of Electro-Codeposited Ni-SiO_2 Nanocomposite Coatings from Deep Eutectic Solvent (DES) Electrolyte

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Abstract:

Metal matrix composites containing metal and semiconductor or insulator nanoparticles have been fabricated through different methods, and mechanical and electrochemical behavior studied [1-8]. Electro-codeposition is a metal matrix nanocomposite coating fabrication method that is used widely due to its superior advantages such as homogeneous coatings, low cost, easy set-up and fast deposition rate [9,10]. Several examples of metal matrix composites are reported in the literature. In the case of nickel-based composites, many of the pure, ceramics and oxides nano/micro-sized particles such as Ti [1], TiO_2 [2,3], SiC [4,5], SiO_2 [6,7], and Al_2O_3 [8] are added as the second phase. In this paper, the fabrication of Ni-SiO_2 nanocomposite coatings and the influence of the addition of SiO_2 nanoparticles on composition, microstructure and corrosion properties of electrodeposited Ni-SiO_2 nanocomposite coatings are discussed. A pulse electro-codeposition method was employed to prepare Ni-SiO_2 nanocomposite coating on the surface of AISI 1045 medium carbon steel from a choline chloride (ChCl)/ethylene glycol (EG)-based deep eutectic solvent (DES) with a ChCl to EG molar ratio of 1/2. Nickel chloride [$NiCl_2.6H_2O$] and 15 g/L silicon dioxide (SiO_2) nanopowder, 10-20 nm particle size and 99.5% purity, were then added to the electrolyte. The electro-codeposition process, for pure Ni and Ni-SiO_2 nanocomposite coatings, was carried out at the same conditions of temperature, current density and frequency that were set to 70 °C, 8 mA/cm^2 and 1000 Hz, respectively. Disc-shaped medium carbon steel substrates were mechanically polished and degreased followed by activation before electrocodeposition. Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), were used to study microstructure, surface morphology, composition, and phase analysis of the Ni-SiO_2 nanocomposite and pure Ni coatings. Corrosion properties of the coatings were evaluated by means of potentiodynamic polarization test in 3.5 wt.% NaCl solution at room temperature. SEM images revealed that the addition of silicon dioxide nanoparticles to the nickel film affects the grain size, microstructure and morphology of the coating surface. The microstructure of the nanocomposite coating is a combination of nano and micro-sized structures on the surface. A granular-like microstructure with a quasi-uniform dispersion of SiO_2 nanoparticles in the coating was observed. Our characterization results confirm the incorporation of SiO_2 nanoparticles into the Ni film. Potentiodynamic polarization results showed that the incorporation of SiO_2 nanoparticles into the Ni film significantly improved the corrosion properties of the coatings compared to the pure nickel. Corrosion potential of Ni-SiO_2 nanocomposite coating increased to a more positive value, and the corrosion current density decreased compared to that of pure Ni. Enhanced corrosion resistance in nanocomposite coating with respect to the pure Ni is explained by the effect of the addition of SiO_2 nanoparticles on both microstructure and composition of the nanocomposite coating. Thus, the electrodeposition method using choline chloride/ethylene glycol-based DES solution can be used to produce Ni-SiO_2 nanocomposite coating with uniformly dispersed SiO_2 nanoparticles in the Ni film that exhibits clearly better corrosion resistance compared to pure Ni coating and suggesting its potential application in industry with the goal of surface corrosion protection.

Keywords: corrosion, nanocomposite, coating, nickel, silicon dioxide, deep eutectic solvent

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Step Towards Highly-Efficient Oxygen Evolution Reaction using nanostructured β-$Ni(OH)_2$

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Oxygen evolution reaction (OER) plays a crucial role in electrochemical energy storage and conversion devices, such as metal-air batteries or unitized regenerative fuel cells, as well as in water electrolyzers [1]. Sluggish reaction kinetics imposes the use of suitable electrocatalysts among which platinum-group metal (PGM) oxides, IrO_2 and RuO_2, have been reported to have the highest activity. Namely, sluggish reaction kinetics results in high overpotential of OER which further results in high energy consumption for water molecule splitting and the overall high price of the process. PGM-based electrocatalysts have high efficiency towards OER, but they also have high price impeding their application in large scale industrial water electrolyzers. Search for lower cost, but highly efficient electrocatalysts for OER is an ongoing quest [2]. Nickel-based electrocatalysts have demonstrated to offer high intrinsic activity along with high stability in alkaline electrolytes [3].

Herein, β-$Ni(OH)_2$ was prepared by hydrothermal method and systematically studied for oxygen evolution reaction in alkaline media (1 M KOH). Material showed activity for OER with low onset potential of ca. 0.55 V and low Tafel slope. Polarization curves were recorded at temperatures up to 85 °C as current industrial electrolyzers commonly operate at temperatures between 65 and 90 °C. Expected reaction kinetics improvement as evidenced by decrease of overpotential and increase of current density reached could be observed for up to 75 °C, while very intense bubbling was observed at 85 °C. Additionally, initial stability test run for 2 h revealed oxidation current density somewhat increasing with time.

Collected results suggest hydrothermally prepared $Ni(OH)_2$ as a good electrocatalyst for OER for application in water electrolyzers and unitized regenerative fuel cells.

Acknowledgments

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Standardless Determination of Nanometric Thicknesses in Stratified Si/C anodes for Lithium-Ion Batteries by Electron Probe Microanalysis

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The present work reports on the development of a standardless method for the determination of nanometric thicknesses for the morphological characterization of anodes of lithium-ion batteries, in particular for those based on binder-free Si/C binary composites generated by sputtering deposition. The procedure was developed based on the detection of characteristic x rays under electron impact, and although it was specifically designed for nano-stratified samples consisting of a Si film deposited onto a C layer (which in turn is deposited on a Cu substrate), it is also easily applicable to other configurations. Since it is necessary to know the thickness of the surface layer to obtain the thickness of the deepest layer, the calculations involve the application of an iterative strategy based on Monte Carlo simulations. The validation of the method was done on a set of samples whose thicknesses were also determined by Rutherford backscattering spectroscopy (RBS), and the method was applied to another set of anodes, which gave results that coincided with the expected values. The thicknesses of the Si and C layers of the binder-free composite anode obtained by the proposed method were used to calculate the specific capacity. Galvanostatic charge-discharge curves up to 100 cycles were analyzed for three different C/Si ratio anodes, and the experimental results were compared with the theoretical capacity for each binary system.

In Figure 1 a particular application example of the developed method is presented. The analyzed samples were prepared by sputtering deposition of three different thicknesses of C onto Cu foils followed by a deposition of a silicon film. The implementation of the method allowed a thickness estimation of 25 nm for Si, and 92, 156 and 190 nm for C. These values were used to obtain the mass ratio of the anode and a corresponding theoretical specific capacity. Afterward, the anodes were mounted as working electrodes in an electrochemical cell with lithium as a counter electrode and cycled 100 times at a constant current of 20 μA. In Figure 2 it is shown, as an example, the cycling response for the electrode Si25/C92 and the corresponding theoretical capacity, 1098 $mAhg^{-1}$, calculated as a reference. The electrochemical test shows that the experimental specific capacity of the particular anode is 1200 $mAhg^{-1}$, in good agreement with the estimation made by the present method. The nano-stratified Si/C anodes prepared by sputtering deposition showed good cycling performance and great stability regarding the silicon volume expansion during the charge-discharge process.

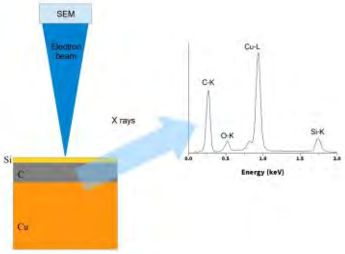

Figure 1

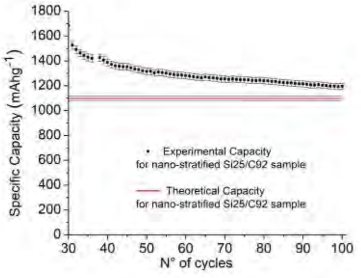

Figure 2

Colorous porous anodic titanium oxide prepared in ethanol-based electrolyte

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Colorous anodic titanium oxide was produced in ethanol-based electrolyte, which contained 0.3 M ammonium fluoride and 2, 3.5, 5 or 10 wt% of deionized water. The new type of electrolyte was describe elsewhere [1]. The applied anodizing voltage was varied between 20 and 60 V and the anodization temperature was kept constant at 20^{o}C.

Morphological characterization of oxide layer was made using SEM (Fig 1). The optical characterization of fabricated samples was done by measuring diffusion reflectance and calculation of theoretical colors. It was found that depending of anodizing conditions the color of fabricated oxides are significantly changed. Moreover, depending of anodization temperature the fabricated anodic titanium oxide have nanotubular or slightly porous morphology. The thickness of oxide is affected mostly by anodizing voltage not temperature. The colors of anodic oxide could be controlled by changing anodizing conditions.

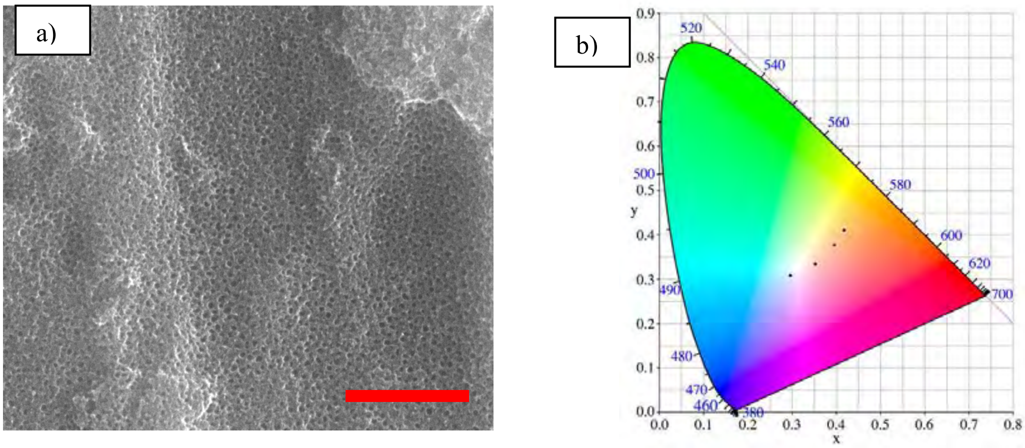

Fig .1. Example of morphology anodic titanium oxide made in ethanol-based electrolyte (a), and theoretical colors of samples made in electrolyte with 3.5 wt% of water (b). The bar is 500µm in real distance.

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Electrochemical pH sensor using tape and paper for oral preventative care

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Low oral pH (<5.5) has been shown to play an important role in dental erosion. The measurement of oral pH can be useful in preventative care, particularly in aiding the dental caregiver in determining the likeliness of future dental cavities. The measurement of oral pH has become a more popular area of research in an effort to develop a more quantitative method for the diagnosis of dental caries. We are developing an electrochemical tape-and-paper-based analytical device for pH measurements. These devices are low-cost, easy to fabricate, disposable and portable. These devices rely on the pH-dependent, redox active species, using intrinsic defects of the material that generate oxogroups on the painted graphite electrode. We have optimized a method to carry out these pH measurements using cyclic voltammetry with the use of an ionic adjuster. By measuring the shift in potentials displayed by these species, we can determine the pH of a sample. We have tested the devices in different buffer solutions as well as commercial pH standards. The electrochemical response of the devices has shown good linear correlation in the tested solutions as well as across multiple devices and different users. The devices show promise for pH measurement in artificial saliva and other oral samples.

Obtaining high-added value products from the technical cashew-nut shell liquid using electrochemical oxidation with BDD anodes

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The electro-organic synthesis is currently experiencing a renaissance due to the tremendous contributions of various electrocatalytic materials as well as the use of electric current as an inexpensive and suitable reagent to drive the electrosynthetic transformations, avoiding conventional chemical oxidizers or reducing agents [1]. Consequently, electrosynthesis has a significant technical impact due to its advantages such as versatility, environmental compatibility (possibility of recovering and recycling non-converted substrates), automation (switching on or off electric current), inherent safety and potential cost effectiveness among others [1]. Although many novel electrode materials have been developed and established in electro-organic synthesis, diamond films (as boron doped diamond (BDD) electrodes) [2] emerge as a novel and sustainable solution in selective electrochemical transformations for value-added organic products. For this reason, in this work, the use of BDD to treat technical cashew-nut shell liquid (t-CNSL) [3] was proposed to favor its conversion on high-added value products such as carboxylic acids [4]. The evolution of five carboxylic acids was followed over time for the experiments of the three different current densities using 0.1% of t-CNSL in 1.00 mol L^{-1} NaOH. At 40 mA cm^{-2}, the most notorious increase in the organic acids concentrations took place during the two last hours achieving electrochemical conversions about of 144, 120, and 75 mg L^{-1} for the acetic, formic and oxalic acids, respectively. The results are discussed in light of the existing literature.

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Photoelectrochemical reduction of CO_2 over Ti-Cu alloys: Effect of phases towards multicarbon products

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Copper species exhibit favorable positions in the conduction band and high potential for reducing compounds adsorbed on its surface [1], being widely studied in the conversion of CO_2 in multicarbon products. However, when applied in photoelectrocatalytic processes, these are easily oxidized and their stability is a challenge. Copper species can be coupled with other materials, such as TiO_2, a n-type semiconductor with excellent charge transfer properties and chemical stability. These oxides in nanostructured size have properties improved and, consequently, obtain better efficiency of photocatalytic activity [2]. Therefore, the present work evaluated the influence of different species and structures of Cu in Ti-Cu system alloys for converting CO_2 in multi carbon products. The electrodes were manufactured to act as photocathodes from Ti-10at.% Cu alloys. These electrodes were prepared using an arc melting and then, annealed at 900 ° C under argon atmosphere during 120 h. After the heat treatment, the alloy was cooled with controlled temperature at 1 ° C min^{-1}. The identification of the phases presents in the substrate was carried out by optical microscopy, diffraction and X-ray dispersion. The Ti– O – Cu nanostructured films were grown by anodic process using a solution of 0.1 M HF in ethylene glycol + 2.5% (v/v) H_2O and heat treated in different temperature within 350 - 550 ° C. The morphological and compositional properties were investigated by scanning electron microscopy and X-ray diffraction. The quantifications of the phases present in each temperature composition were carried out by the Rietveld method. The photoelectrochemical characterization was examined by linear sweep voltammetry in N_2 bubbled 0.1 mol L^{-1} Na_2SO_4 aqueous solutions (pH 6.6) under irradiation of chopped UV and visible light (a 150 W Hg lamp), with a potential range of onset potential to -1.0 V *vs.* Ag/AgCl/Cl (3M). The photoelectrocatalytic reduction experiments were carried out bubbling CO_2 into 0.1 mol L^{-1} of $NaHCO_3$ aqueous solution and a potential at -0.5 V was applied. The electrode was illuminated for 3 h and then, the samples were taken each 0.5 h to evaluate the product formation at different times. The determination and quantification of compounds, such as methanol, ethanol, and acetone were conducted by gas chromatography by flame ionization. On the substrate, the analyses showed Ti_2Cu and $TiCu_3$ intermetallic phases in its composition. The presence of a significative quantity of Ti_2Cu precursor was essential to defined film composition and its photocatalytic behavior. The Rietveld quantification method for these electrodes revealed binary and ternary oxides on the film nanostructured in different compositions for each temperature. The presence of ternary oxide derives from Ti_2Cu precursor which can provide other properties to the electrode, as more stability and high redox potential. Some characteristic that can be attributed to the Ti_2CuO is oxygen sharing between Ti and Cu species, that did not allow the copper dissolution and change its oxidation state, consequently, it gave new properties for this material that provided significant concentrations of methanol and ethanol as final products.

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Hybrid Static/Flowable Electrodes

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In contemporary redox flow batteries, either static or flowable electrodes are conventionally used. Although the conductivity in static electrodes is several orders of magnitude higher than that of a flowable electrode, the latter offer distinct operational advantages, such as dendrite-less metal deposition.

We here report on a new method utilizing a flowable electrode that can operate in both static and flowable modes, with the user deciding the mode during cell operation. The latter technique utilizes gravitational forces acting on particles to form either a flowable fluidized bed electrode or packed electrode.

We show that such an electrode can repeatedly cycle between modes by adjusting electrode flow velocity, allowing for over four orders of magnitude variation in electric conductivity as seen in Figure 1 .

We further demonstrate the discovery of a novel operational regime, at intermediate velocities where large-scale particle motion through vortex formation occurs, which enables exceptionally high electric conductivity in the flowable state.

We expect this new approach could enable the creation of a more versatile electrodes which can form the basis of future electrochemical systems for energy storage, conversion or water desalination.

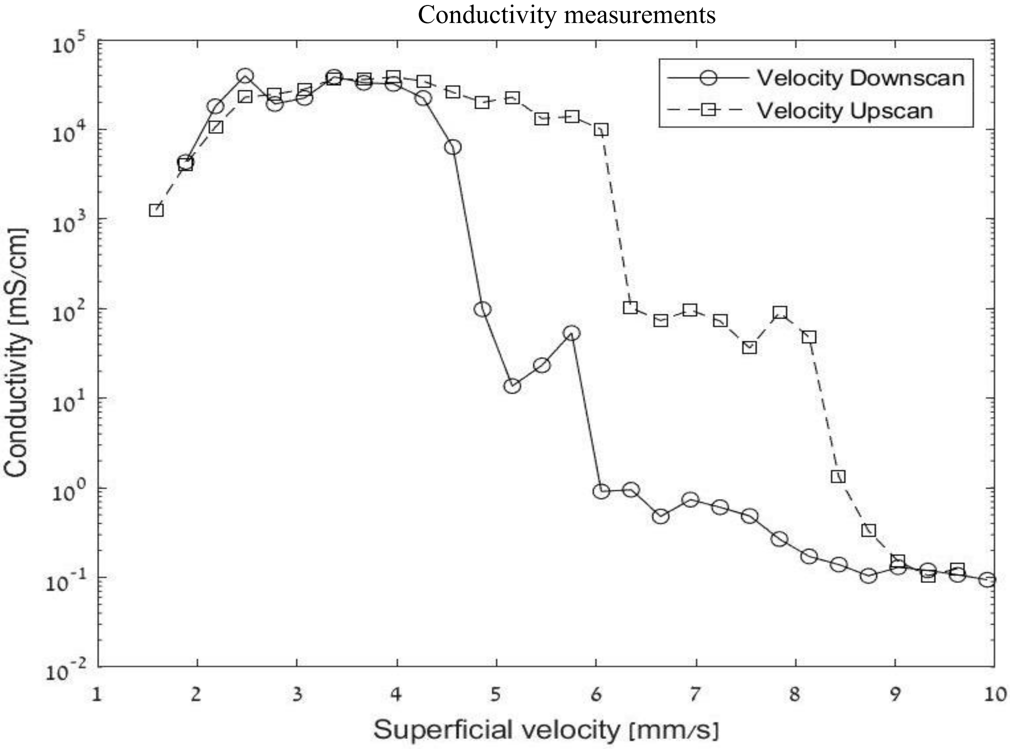

Figure 1 - Electrode Conductivity Vs. Superficial velocity. The electrode changes its state from flowable to static and back exhibiting a change of over 4 orders of magnitude in its conductivity

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Development of Anaerobic Biocathodes with Polymer-modified Gas Diffusion Electrodes for Converting CO_2 to Organic Compounds via Microbial Electrosynthesis

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In the last few years, bioelectrochemical systems (BES) have shown great potential for the conversion of CO2 into C2-C6 volatile fatty acids (VFAs) and alcohols. Despite their versatility, BES present limitations such as the long time associated with the development of biocathodes and the start of bioproduction, even in presence of a pre-enriched inoculum. In this work, we studied the conversion of CO2 via microbial electrosynthesis in BES equipped with carbon based gas diffusion electrodes (GDEs) modified with hydrophilic and conductive polyaniline (PANI) polymer. Reactors were inoculated with a pre-enriched inoculum and operated at -1000 mv vs Ag/AgCl. The utilisation of PANI-modified GDEs significantly reduced the start-up time of bioproduction to only 6 days with an acetate concentration of 1.29 ± 0.36 g L-1 after 17 days of operation, and of 4.01 ± 0.5 g L^{-1} after 24 days with apparition of butyrate. On the other hand, BES reactors equipped with non-modified GDEs showed much slower start-up (17 days) reaching 0.33 ± 0.12 g L^{-1} after 24 days and 1.19 ± 0.73 g L^{-1} after 31 days. Reactors were operated during 60 days and PANI-GDEs led to an acetate concentration of 6.85 ± 0.9 g L-1 and 0.20 ± 0.05 g L-1 butyrate. Electrochemical and physico-chemical analysis revealed that the PANI polymer enhances the interaction between the biofilm and the electrode, thus contributing to the fast start-up and higher bio-production compared to non-modified carbon cloth GDEs.

On the electrochemical behavior of kraft black liquor using BDD electrodes

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Black liquor (BL) is a complex solution generated as a by-product of the kraft pulping process and is mainly composed of inorganic salts, such as NaOH, $NaCO_3$, and Na_2SO_4, and lignin [1]. In the last few years, there has been a growing effort of the scientific community to understand the electrochemical behavior of the BL [2–4]. As the electrolysis of BL is being more explored it is being pointed out as a promising process to the treatment and valorization of this by-product. In fact, understanding this electrochemical behavior can bring an important development for the wastewater/environmental processes of pulp and paper industries [5–7].

Therefore, this work aims at analyzing by voltammetric (cyclic voltammetry, CV), amperometric (chronoamperometry, CA), and potentiometric (chronopotentiometry, CP) techniques the behavior of kraft BL solutions utilizing boron-doped diamond (BDD) electrodes. CVs are recorded at several scan rates and the peaks are analyzed using the Randles-Sevcik equation. Then CA and CP techniques are run, and the results analyzed in order to better understand the electrochemical oxidation of lignin in the BL. The obtained results are critically discussed and compared with previous literature studies to comprehend the catalytic effect of BDD electrodes in the electrooxidation process of the lignin present in the kraft BL.

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Synthesis and spectroelectrochemical analysis of P3HT/PCBM and CP3(HT-OT)/PCBM blends.

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Poly(3-alkylthiophenes) (P3AT´s), due to their double conjugate bonds, are part of the group of conducting polymers, which are of great interest for applications such as battery electrodes, organic light emitting diode (OLED) electronic devices, organic solar cells, low-cost integrated circuits and organic field effect transistors, owing to their good stability, high conductivity and flexibility of preparation[1]. After electrochemical synthesis, these polymers can change from insulators to conductors due to reversible oxidation processes in the p conjugate system, resulting in chains with positive charges, polarons and bipolarons, which are balanced by the incorporation of counterions (anions), referred to as *p*-type doping. Films obtained in this way exhibit properties that make them efficient electron donors at heterojunctions with n-type materials, such as fullerenes and its derivatives, used in organic solar cells.

To study the electrochemical properties of modified polymeric films, the electrochemical impedance (EIS) could be combined with vibrational spectroscopy in order to understand how the positive segments in polymer matrix affect the process of electronic transport in those materials, such as double layer capacitance, charger transfer velocity, charge transfer process[2].

Therefore, in this work, first, a poli(3-hexylthiophene), P3HT, and a blend obtained from two 3-alkylthiophenes monomers, 3-hexylthiophen and 3-octylthiophene, named as CP3(HT-OT), were synthesized by chronoamperometry (in non-aqueous media)[1]. After this, under both films, were deposited, by dropping coating method, a fullerene derivative, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). Thus, the blends formed between the P3AT's and PCBM, named as P3HT/PCBM and CP3(HT-OT)/PCBM, were characterized by cyclic voltammetry (CV), EIS, XPS (X-ray Photoelectron Spectroscopy), photoluminescence (PL) and *in situ* and *ex situ* Raman spectroscopy.

The presence of PCBM in P3HT and CP3(HT-OT) blends were confirmed by XPS, which demonstrated a small difference of the fullerene derivative between them. PL spectra showed a *quenching* because of a successful heterojunction formation, being more effective in P3HT/PCBM (indicating that, in this blend, the charge transfer process were more effective). The presence of PCBM did not significantly alter the *band gap* of the blends but was able to change the relative quantity of positive segments, evaluate by in situ Raman spectroscopy, in polymer matrix. The addition of PCBM increased the *bipolaron* segments in P3HT, while in CP3(HT-OT) stabilized the *polaron* segments, considering the submission of the blends to anodic potential (from 0 to +1,4 V). In addition, EIS showed that, despite the reduction in charge resistance transfer (R_{CT}), 9% and 47% for P3HT/PCBM and CP3(HT-OT)/PCBM, respectively, due to the stabilization of positive segments, the non-homogenous phase separation of P3AT's and PCBM prevented this reduction from being even greater.

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Study of Methanol electrooxidation on Thin Nickel Films by Sampled Current Voltammetry

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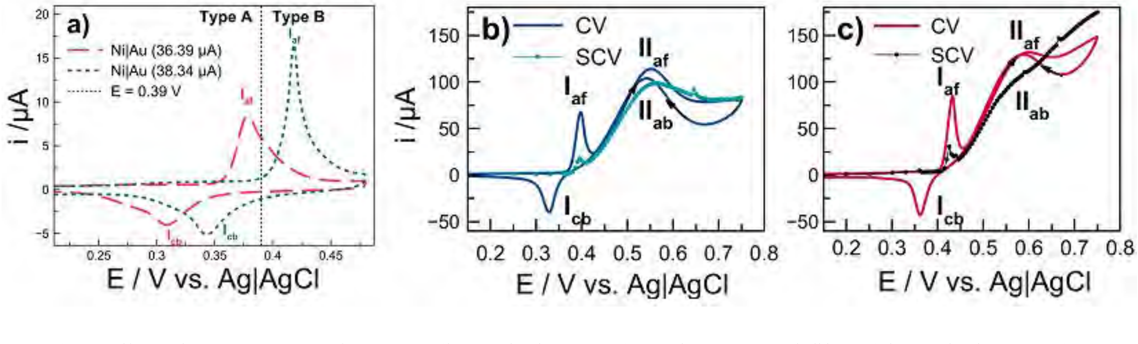
Because its application on direct methanol fuel cells [1], several works have focused on the synthesis of materials with electrocatalytic activities comparable to that of platinum. Salinas et al. [2] showed that Ni films deposited on Au under galvanostatic control had high electrocatalytic activity. In this work, Ni films were deposited by the galvanostatic method on gold electrodes. Their electrocatalytic activity for methanol electrooxidation was evaluated by cyclic voltammetry (CV) and sampled current voltammetry (SCV). The sampled voltammograms were constructed from individual chronoamperometric measurements so that each measurement was made with a renewed surface, eliminating the effects of the electrode history present in voltage sweep methods [3].

Electrodeposition results of two processes, nucleation and growth, occurring at two different time scales. Nucleation proceeds at the millisecond timescale, and the diffusion field follows the microscopic features of the electrode's surface. The growth of the nuclei takes place at longer timescales when the diffusion field has extended, so the geometric area controls it. Therefore, the applied current relative to the electroactive area dictates nucleation conditions, but leads to different growth kinetics, resulting in variability on the Ni deposits, determining the predominance of $Ni(OH)_2$ polymorph. Figure 1a shows the Ni deposits after cycling in 1 M KOH. The position of the NiOOH peak (Iaf) changed depending on the total applied current. For simplicity, two types of Ni films were identified: Type A with the NiOOH formation peak located below 0.39 V vs. Ag|AgCl, and Type B, which has the NiOOH formation peak above that threshold value. The solid lines in Fig. 1b and 1c represent the CVs for Ni films obtained in the presence of 0.5 M methanol. The anodic peaks, IIaf and IIab, correspond to methanol oxidation during the forward and backward scans. The sum of the current peaks, called Electrocatalytic Intensity, *EI*, can be used to evaluate Ni films' activity. Accordingly, Type B deposits show higher activity for methanol electrooxidation compared to Type A. However, the superimposed SCVs (dotted lines) suggest that although Type B films are suitable catalysts for methanol oxidation, they also exhibit high activity for oxygen evolution, as evidenced by the current increase beyond 0.5 V vs. Ag|AgCl. Conversely, the Type A deposit shows high activity for methanol oxidation without oxygen evolution interference, making it a suitable material for direct alcohol fuel cells. These results demonstrate that SCV is a valuable technique to gain insight into the catalytic behavior of electrocatalytic materials.



a) Cyclic voltammogram of Type A (long-dash curves), and Type B Ni films (short-dash curves). Scan rate: 50mV s^{-1}, 1 M KOH. (b) Cyclic voltammograms (solid lines) and (b) sampled current voltammograms (dotted lines) of Type A and Type B films in 1 M KOH + 0.5 M methanol

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Dye Doped Silica Nanoparticles for Efficent Electrochemiluminescence Imaging

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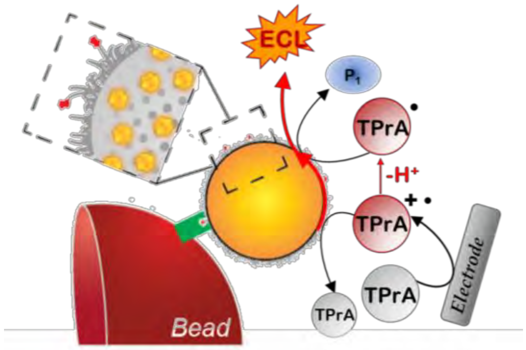
Electrochemiluminescence (ECL) is a leading technique in bioanalysis.[1] Since the excited species are produced with an electrochemical stimulus rather than with a light excitation source, ECL displays improved signal-to-noise ratio compared to photoluminescence, with minimized effects due to light scattering and luminescence background.[2]
Chasing ever-increasing sensitivities, ECL can ideally be coupled to nanotechnology and supramolecular chemistry to develop new systems and strategies for analyte determination also in very complex matrices.[3,4]
In particular, dye-doped silica nanoparticles (DDSNs) present many advantages: they can be obtained with accessible synthetic schemes, are intrinsically hydrophilic, and, thanks to silica chemistry, are prone to bioconjugation. With this approach we were able to achieve extremely bright systems and DDSNs assume the photophysical properties of the dye accumulated within the nanoparticle.[5] In DDSNs, light emission is influenced by the combination of several factors that make DDSNs complex multichromophoric structures. However, when ECL comes into play, the scenario is even more complicated due to the coreactant−NP interactions effect.[5] Such complex scenario was approached at the theoretical level by developing suitable mechanistic models for ECL generation[6] while, at the same time, the influence of doping level on ECL efficiency was evaluated. Our results showed that the ECL intensity of a nanosized system cannot be merely incremented acting on doping, since other parameters come into play. These studies provide valuable indications for the design of more efficient ECL nano- and micro-sized labels for ultrasensitive bioanalysis.



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The hydroxylation of o-quinone as a kinetic model to the formation of 6-hydroxy-dopamine.

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Nowadays, mental disease diagnosis increases significantly in society in general. [1] The causes of diseases such as Parkinson's disease, Alzheimer's, schizophrenia and depression remain to be unveiled in detail. In this particular scenario, dopamine (DA), is involved in some pathways which are related to synapsis and signalling functions. Most of DA's functions are related to its redox reactivity, which can be electrochemically simulated in an EECEE mechanism.[2] Following-up to the oxidation of DA's catechol moiety to o-quinone, a chemical step occurs as the molecule undergoes an intramolecular Michael addition, a cyclization. [2] On the other hand, the follow-up cyclization reaction competes with the intermolecular Michael addition which would generate the 6-hydroxy-dopamine (6-OHDA). This secondary product (6-OHDA) is used in animal models to generate Parkinson's disease in the subjects. [3] Since DA also presents the cyclization reaction, catechol (CAT) was used as a model to observe the extension of the Michael addition at physiological pH, therefore simulating the *in vivo* DA behaviour in an *in vitro* situation. Cyclic voltammetry was used to obtain the kinetic rate constant (kf) of the chemical step which follows-up the CAT oxidation at physiological pH and other pH values using the number of effective electrons [4] to better comprehend the intermolecular addition mechanism. The Tafel plots were obtained to observe the mechanism as a function of the scan rate, since the charge transfer coefficients (β) values are sensitive to the mechanism change, as already demonstrated. [2] The scan rate values were then restricted in an appropriate window and the kf values to the addition were then obtained. In sequence, to observe the extension of this reaction, the kf values obtained were compared to a recent study of our group in which the cyclization rate constant of DA in pH = 7.4 was obtained. The results show that CAT intermolecular addition occurs with a kf = 0.28 s^{-1}, which is 0.04 s^{-1} superior to the 0.24 s^{-1} previously reported for DA's cyclization. In addition, the chemical step for CAT presented a parabolic behaviour, with a peak at approximately 7.4, which allows two conclusions. Firstly, that the reaction occurs at its optimized situation in physiological media., Secondly, that after CAT oxidation, the further nucleophilic addition occurs in a similar mechanism to a S_NAr, which could also be the case for the 6-OHDA formation. [5]

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Electrochemical and magnetic properties of green synthesized Fe_2O_3 maghemite nanoparticles

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Green synthesis of iron nanoparticles has accumulated an ultimate interest over the last few years due to their distinctive properties and applicability in various fields of science and technology. The use of biological products such as microorganisms, plant extracts or plant biomass is proving to be a better alternative to chemical and physical methods for the engineering of metal oxide nanoparticles through environmentally benign routes. In the present study, the synthesis of iron nanoparticles (Fe_2O_3) was achieved using coffee extracts. The synthesized materials were studied using X-ray diffraction (XRD), UV-visible spectroscopy (UV-vis), Fourier Transform Infrared (FTIR) Spectroscopy, Vibrating Sample Magnetometer (VSM), High Resolution Scanning Electron Microscopy (HRSEM), High Resolution Transmission Electron Microscopy (HRTEM) and Cyclic voltammetry (CV). The average diameter of the Fe_2O_3 nanoparticles was observed to be approximately 35 nm while HRTEM confirmed the cubic nature of the nanoparticles. The FTIR spectrum of the nanoparticles revealed the role of the biomolecules present in the extract in capping the nanoparticles with prominent bands at 3381 cm^{-1}, 1384 cm^{-1} and 691 cm^{-1}. UV-vis studies revealed an absorption band in the ultraviolet region of 289 nm indicating confirming the successful development of the prepared nanoparticles as also indicated by the optical energy band gap determined using Tauc plot. The VSM studies showed the ferromagnetic nature of the synthesized nanoparticles and CV illustrated the electrochemical behaviour of the Fe_2O_3 nanoparticles on glassy carbon electrodes. The modified electrode with showed good electron conductivity when compared to the bare electrode an indication of the potential use of the nanoparticles in the development of sensors or biosensors.

Sensitive and Selective Detection of Low-Level Ammonia Gas Sensor by Reduced-Graphene-Based Nanocomposie

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Ammonia is an important indicator for the environment quality and agriculture safety applications. It also has been identified as an important biomarker of breathing gas, and the elevated ammonia levels in exhaled breath could be the results of liver or kidney-related desieases. The exhaled ammonia gas concentration for healthy human is down to 0.02-2 ppm [1], and for the environmental quality evaluation should be lower to 50 ppb. Due to the low concentration and the complicate sample gases, it is important to develop a highly sensitive and selective ammonia sensor. Several materials such as metal oxide, conducting polymer and carbon nanomaterials have been extensively used for ammonia gas sensing. Among those materials, carbon-baed nanosomposite holds great promise for low-concentration ammonia sensing.

We demonstrated a highly sensitive and selective ammonia sensor based on reduced-graphene nanocomposite for detection of ammonia down to the ppb-level at room temperature. Tungsten oxide and polyaniline was incorporated into easily functionalized reduced graphene in supercritical fluid to form a nanocomposite. Metallic nanocatalyst was doped to enhance the sensitivity and selectivity. Ammonia adsorbed on the sensing membrane and then be oxidized at room-temperature. Therefore, the resistance of sensing membrane increased with ammonia concentration. The sensor could detect the ammonia concentration in the range from 0 to 100 ppm at room temperature. The sensitivity was enhanced 4 times by the nanocatalyst, and the lower detection limit was 50 ppb. The effect of interference gases, including nitric oxide (NO), carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2) has been evaluated as well, and all the cross-talk was less than 10%.

Furthermore, ammonia gas is highly water soluble, the sensing resistance was shift significantly by humidity, especially in higher humid atmosphere. In order to solve the problem, the electrode surface was more hydrophobic. After surface modification, the humidity effect decreased. The sensing mechanism of electrode and effect of humidity was also investigated. The experimental result suggested that the catalyst doped nanocomposite had high sensitivity, stability and selectivity for low concentration ammonia sensing at room temperature, the influence of humidity has been overcome by the surface modification. A room temperature operated low-level ammonia sensor could be potential applied for exhaled gas or environmental quality monitoring.

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Ag doped black TiO_2 nanocomposite with enhanced photocatalyst abilities for organic pollution degradation under visible light

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The development of noble metal doped on semiconductor materials has attracted significant attention [1, 2]. Herein, the degradation of Methylene blue over Ag doped black TiO_2 nanocomposite, synthesized using a simple electrochemical doping method, was reported. The Ag nanoparticles doped on black TiO_2 nanotubes exhibits a superior degradation efficiency of methylene blue aqueous solution under visible light irradiation. The efficiency is up to 75%, and around 4 times higher than that of pure TiO_2 nanotube arrays. The enhanced photodegradation performance is attribute to the formation of surface plasmon resonance caused by Ag nanoparticles, as well as the conductivity enhancement caused by Ti^{3+} and Ag doping. This nanocomposite can effectively increase photocurrent under irradiation of visible light and improve the photocatalyst efficiency of TiO_2 nanotube [3].

Reference

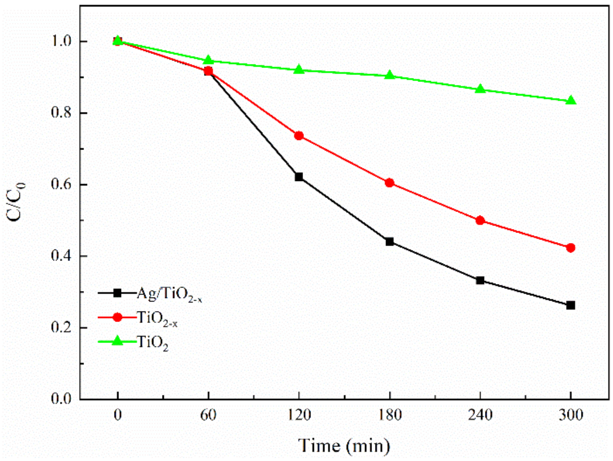

Figure1 Photocatalytic degradation of MB using different catalyst

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Neuronal Tau Protein Film Stability on Gold Surface: Electrochemical Impedance Spectroscopy and Cyclic Voltammetry Studies

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Tau is a neuronal protein responsible for microtubule formation [1]. It is also the pathological protein active in the Alzheimer's Disease (AD) pathway. When Tau begins to aggregate as a result of misfolding, the neuronal cells die due to the lack of microtubule formation and can take on prion-like properties [2]. Therefore, detection of aggregated Tau can serve as a powerful tool in the early diagnosis of AD and dementia related diseases. As has been previously demonstrated, Tau 441 can be detected with an electrochemical immunoassay based on the electrochemical impedance spectroscopy (EIS) by using gold electrode [3]. The EIS was also used to monitor interactions between Tau protein and Heparin [4]. Due to the sensitive nature of protein molecules, buffers of physiological pH need to be employed to maintain native protein structure. However, not all buffer solutions are appropriately suited for surface studies. Herein, we describe use of EIS and cyclic voltammetry (CV) to monitor and detect surface stability of Tau protein films on gold electrode in two common buffers: MES buffer and Phosphate Buffer (PB). After modifying the surface of the electrode with activated lipoic acid and Tau, a series of further incubation steps were performed to test surface stability under various conditions. The EIS and CV were measured as a function of Tau or Heparin concentrations, and incubation time and temperature. The control experiments included, Tau-free surface, Heparin-free solution, and buffer solutions in order to minimize non-specific interactions. The stability of the surfaces was measured as a signal change in EIS and CV after incubations and it was discovered that certain buffered solution induced large changes in tau protein films on surfaces.

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Operando Surface Structure Determination of Pt(111) under Realistic Oxygen Reduction Conditions using High-Energy Surface X-Ray Diffraction

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Platinum is the most widely used electrocatalyst driving water-splitting and (the reverse) hydrogen oxidation reactions, which are the processes occurring in electrolysers and fuel cells, respectively. Due to the material costs, it is of crucial importance to maximize the electrode stability. Experiments under static, oxygen-free conditions have provided a detailed description of the degradation of the Pt(111) electrode surface by applying highly oxidizing potentials. In our High-Energy Surface X-Ray Diffraction (HE-SXRD) experiments we have shown that the Pt(111) surfaces change significantly at potentials above 1.1 V vs RHE. These changes depend on the potential, its scan rate and for how long it is applied. Despite extensive oxidation of the electrode, we did not observe any features indication the formation of an ordered (surface) oxide.

However, it is unclear how this degradation changes in case of a high oxygen chemical potential as during the oxygen reduction reaction. We have developed a Rotating Disk Electrode (RDE) setup that can be mounted on the beamline diffractometer, enabling us to perform operando HE-SXRD experiments. This setup has been used to determine the structure of a Pt(111) while a large current density for oxygen reduction is applied. The results are compared to measurements performed under static and oxygen-free conditions.

Reduction of Methane Emissions by Living Electric Cables

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Cable bacteria are living electrochemical devices using internal wires to direct electrons from anaerobic decomposition of organic matter to oxygen reduction via a sulfur shunt in sediments. The sulfur shunt involves a continuous cycling between electrogenic sulfide oxidation by cable bacteria und sulfate reducing bacteria, leading to an overall accumulation of sulfate in the porewater.

Here we show that the exclusion of cable bacteria led to the direction of the electron flow to methanogenesis resulting in a more than tenfold higher methane emission from rice-vegetated soil pots to the atmosphere. We also found that cable bacteria do naturally occur in rice fields - although thriving well in some fields, they appear to be absent in others. Moreover, the cable bacteria-induced effects potentially include the protection of rice plants against toxic sulfide. Taken together, we suggest that unraveling the factors controlling cable bacteria blooms in rice fields would allow to tailor mitigation strategies to reduce methane emissions and sulfide toxicity in rice fields.

Ion Exchange Involving Graphene Oxide and Metallic Cations as a Tool for the Electrosynthesis of Advanced Materials

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Prussian blue is a hexacyanometallate mixed-valence complex constituted by iron metallic centers in oxidation states two and three, connected by bridges of cyanide ligands. Iron centers can be replaced by other transition metals, generating a class of compounds with the same structure of Prussian blue, the so-called Prussian blue analogues (PBA), with the formula $A_xM_y[M'(CN)_6]_z{\cdot}nH_2O$, wherein M and M' are transition metals and A is a metal cation. These complexes present unique electrochemical properties. At the same time, they show low electrochemical stability, which can be improved through the preparation of composites with carbon nanostructures like graphene or carbon nanotubes. [1,2] This work presents a novel, simple and efficient route to prepare thin films of PBA/graphene nanocomposites, based on ion-exchange reactions. Thin films of graphene oxide (GO) were prepared through the liquid-liquid interfacial route developed in our research group.[3] The GO films were deposited over Fluor-doped tin oxide covered glass (FTO/glass) and immersed in 0.1 mmol L^{-1} aqueous solutions of Fe^{3+} or Cu^{2+} ions for different time intervals, aiming ion-exchange reaction between acidic hydrogens of GO surface and the metallic ions in solution. Further, the films were washed several times with water and reacted with aqueous solution of $NaBH_4$. The reduction process converts graphene oxide into reduced graphene oxide (rGO) and cationic species into their metallic forms. In the following, these films have been used as precursor for both Cupper hexacyanometallates (CuHCF) or iron hexacyanometallates (FeHCF) composites, through heterogeneous electrochemical reactions with $[Fe(CN_6)]^{3-}$ aqueous solution, in a three-electrode electrochemical cell in which the ion-exchanged rGO films act as work electrodes. The cyclic voltammograms of the films during the deposition reactions show redox processes in the region of 0.7 V for Cu^{2+} and 0.8 V for Fe^{3+}, in which the current intensities increase according the number of cycles, indicating the Prussian blue and PBA formation. The occurrence of FeHCF and CuHCF was confirmed by Raman and FT-IR spectroscopy. The morphology of the films visualized by scanning electron microscopy shows the formation of cubes homogeneously distributed over the entire rGO film after electrodeposition, which indicates the formation of hexacyanometallates. The results demonstrate the viability of the electrodeposition processes and represents a new route to prepare PB- and PBA-based composites thin films, opening several possibilities for application in different fields.

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Electron microscopy of lignin from electrooxidation of kraft black liquor

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Black liquor (BL) is a complex solution generated as a by-product of the kraft pulping process and is mainly composed of inorganic salts (such as NaOH, $NaCO_3$, and Na_2SO_4), and lignin [1]. In the last few years, there has been a growing effort in the scientific community to understand the electrochemical behavior of the BL [2-4]. Currently, there are some well-known processes for the recovery of the lignin, such as the noteworthy LignoBoost and LignoForce commercial processes, a sequence of acidification steps used for the precipitation of the lignin present in the black liquor [5,6]. However, the method used for lignin extraction has a direct impact on the properties of the lignin obtained. As such, it is important to select the appropriate method for the lignin intended applications. As the electrolysis of BL has been more explored in the last few years and can be a promising process to the treatment of this by-product, understanding the properties of the obtained lignin by electrolysis poses an important challenge for its commercial valorization [7].

This work aims to analyze by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques the lignin obtained by electrolysis of kraft BL samples utilizing nickel electrodes. To the best of the authors' knowledge, this is the first time that differences between lignin samples are assessed by electronic microscopy. SEM images, coupled with energy dispersive X-ray analysis, are obtained for several samples of lignin collected from kraft BL by different extraction processes. The morphology of each different sample is critically analyzed. TEM analysis is also performed in the same samples to assess the particle size distribution and understand possible differences in the structure of each lignin sample. The results obtained for the electrodeposited lignin are discussed and compared with those of commercial lignin samples. This will allow us to better comprehend the characteristics of the lignin obtained during the kraft BL electrolysis process.

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Preparation and characteristics of a glassy carbon electrode modified with multi-walled carbon nanotubes and palladium

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Glassy carbon due to its unique properties such as high electrical and thermal conductivity, hardness, resistance to high temperatures, chemicals and stability in a wide range of polarization potentials is a widely used electrode material in electrochemistry. In order to improve or obtain new properties of the electrodes surfaces, inter alia, the glassy carbon electrode is subjected to various modifications. Surface modifications can be carried out, for example, as a result of electrochemical processes (electrodeposition of polymers or metallic layers) as well as by applying new materials to the surface (e.g. carbon nanotubes, graphene).

Carbon nanotubes are one-dimensional structures characterized by high electrical conductivity, high chemical stability, high electrical conductivity, high surface area-volume ratio, high adsorption capacity resulting in increased sensitivity of sensors. They are used as a material for modification of electrodes surfaces which are at the same time a substrate for metallic catalysts.

Palladium due to its catalytic properties and hydrogen sorption capacity is used to build fuel cells operating on the basis of oxidation of small organic compounds, such as methanol or formaldehyde.

The type of electrode, surface development and microstructure as well as the size and dispersion of the catalyst on the electrode surface strongly affects the work of such a cell and its efficiency. The combination of the above-mentioned materials, namely: glassy carbon, carbon nanotubes and palladium, results in obtaining an electrode with new properties.

The aim of presenting work was to obtain glassy carbon electrodes (GCE) modified with multi-walled carbon nanotubes (MWCNTs) and palladium (GCE/MWCNTs-Pd), to characterize them in terms of surface morphology and to study their electrochemical properties.

The preparation of GCE/MWCNTs-Pd electrodes consisted of applying multi-walled carbon nanotubes to the prepared glassy carbon electrode surface and electrochemical generation of palladium nanoparticles with programmed charges (-0.005, -0.020, -0.050 and -0.100 C). GCE/MWCNTs-Pd electrodes with different content of palladium nanoparticles were characterized in terms of surface morphology using atomic force microscopy (AFM) and scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDS). However, the evaluation of electrochemical properties was carried out with use of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in the environment of perchloric acid.

As a result of electrochemical Pd catalyst generation, palladium nanoparticles were obtained in four size ranges: 10-30, 20-40, 50-60 and 70-90 nm. Based on the obtained measurement results, it was observed that the quantity and size of the obtained nanoparticles of deposited palladium on the electrode depends on the charge used during the electrodeposition. The resistance of GCE/MWCNTs-Pd electrodes decreases with increasing amount of palladium.

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Unveiling the origin of carbon dilatometric changes with the application of novel SPECS technique

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Many researchers have been studying the ions migration in the activated carbon porous structure to date. One direction of these studies focuses on the examination of dilatometric changes in polarized electrodes. It was found that depending on the current direction, the response of the electrode is different and cathodic polarization causes more pronounced changes. Our recent findings, with application of the electrochemical contact angle measurement, allowed us to observe the direct electrolyte adsorption on the polarized electrode surface. Collected data followed the established trend, where a cathodic polarization induces better wettability and faster absorption.

Now, to further understand the nature of the ion migration in the porous structure of carbon electrode, we applied the dilatometric measurement combined with novel Step Potential Electrochemical Spectroscopy (SPECS). By merging these two techniques, we were able to analyze and identify the current derivatives resulting in specific electrode behavior. Thus, the overall current response has been deconvoluted to individual components.

For this research, two commercial carbons, i.e., Kuraray YP-50F with "closed" and Cabot BP2000 with "open" porosity was chosen. $[EMIm]^+[TFSI]^-$ ionic liquid (IL) was selected as the electrolytic solution. The application of this IL was intentional, as the size of cation and anion are similar. Moreover, the selection of IL electrolyte limits the possibility of parasitic redox processes that may contribute to the final result.

Briefly, it seems that the dilatometric changes depend on the type of the porosity rather than the size of the ions. Moreover, it is assumed that the volume of ions is less important than their mass and mobility during polarization. However, the current deconvolution suggests a non-linear dependence between the 'diffusion' and 'geometric' components.

Finally, the presented results will elucidate the reasons that stay behind the differences in ion diffusion into the carbon porous structure.

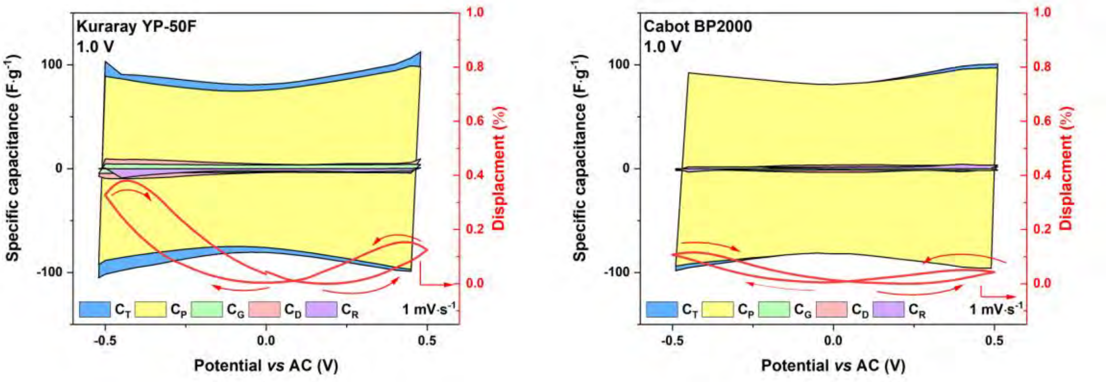

Figure: The SPECS current deconvolution and recorded corresponding dilatometric changes
C_T – Total, C_P – Porous, C_G – Geometric, C_D – Diffusion, C_R – Residual

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Maleic acid from furfural via a cascade approach combining photochemistry and electro- or biochemistry

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Maleic acid is an important raw material that finds multiple applications in the chemical industry such as in manufacturing of unsaturated polyester resins, lubricant additives, surface coatings, textile, photographical chemicals, plasticizers, pharmaceutical products and in agricultural chemicals. In our on-going research, Maleic acid is widely being used to synthesize chemicals for different applications, biobased aromatic (bulk) chemicals in particular.[1]

The current industrial process of maleic acid involves hydrolysis of maleic anhydride which in turn is obtained from the vapor phase oxidation of fossil-based benzene or n-butane. Lately, renewable resources have been investigated to circumvent the use of fossil derived feed-stocks. In particular, biomass-derived platform chemicals like butanol, levulinic acid, 5-hydroxymethylfurfural and furfural were investigated as starting materials for the synthesis of maleic acid.[2] Among these platform chemicals, furfural is an interesting substrate since the commercial production is already established starting from carbohydrates.[3]

In the present study, we investigate the two-step synthesis of maleic acid under very mild conditions. In the first step, 5-hydroxy-2(5H)-furanone is synthesized via photochemical oxidation and proposed as an stable intermediate. Subsequent oxidation in the second step, either by an electrochemical or enzymatic process, to produce maleic acid in high yield and selectivity.

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$Zn_{1-x}Co_xO$ *vs* Ag-ZnO Photoanodes Design Via Combustion: Characterization and Application in Photoelectrocatalysis

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In this work different synthetic conditions were analyzed for the preparation of modified ZnO photoelectrodes, in order to prevent the recombination of their photogenerated charge carriers and allow the continuous formation of electrons and holes on photoelectrocatalytic reactions [1,2]. This study aims to prepare in a simple and proficient way photoelectrodes of the ZnO chemically modified with cobalt, $Zn_{1-x}Co_xO$ and superficially with silver Ag-ZnO, both produced from combustion synthesis process and deposited on the indium tin oxide conductive surface by casting method. The influence of different percentages of the metal nitrate precursors (either Co or Ag – 2.0% mol L^{-1}) and thermic treatment (either 500 or 600 ºC) on the photoelectrochemical response of the prepared electrodes were analyzed. The photoelectrodes were used in a photoelectrochemical discoloration reaction of methylene blue (MB) dye. X-ray diffraction (XRD) analysis confirmed chemical modification of ZnO with cobalt and superficial modification with silver for all samples (Fig. 1-a). Scanning electron microscopy indicated that the sample with 2.0% metallic modifying agent and treated at 600 °C produced smaller-sized particles for both materials. Therefore, the electrodes prepared by this condition were the ones that provided better photoelectrochemical and photoelectrocatalytic responses for the MB discoloration, $Zn_{1-x}Co_xO$ (132 μA cm^{-2} and 9.05×10^{-3} min^{-1}) and Ag-ZnO (162 μA cm^{-2} and 15.0×10^{-3} min^{-1}) (Fig. 1-b,c). The surface area related to the particle size and their morphology were determinant factors for the photoelectrodes efficacy. The significant increases in current density, j_N, and photoelectrocatalytic, k_{obs}, efficiencies for Ag-ZnO electrodes are attributed to the synergism between the ability to remove and store electrons by Ag with the applied potential, thus significantly hampering the recombination of ZnO charge carriers under UV light. The superficial modification of ZnO with silver is more efficient for the inhibition of ZnO photogenerated exciton recombination, when compared to the chemical modification with cobalt.

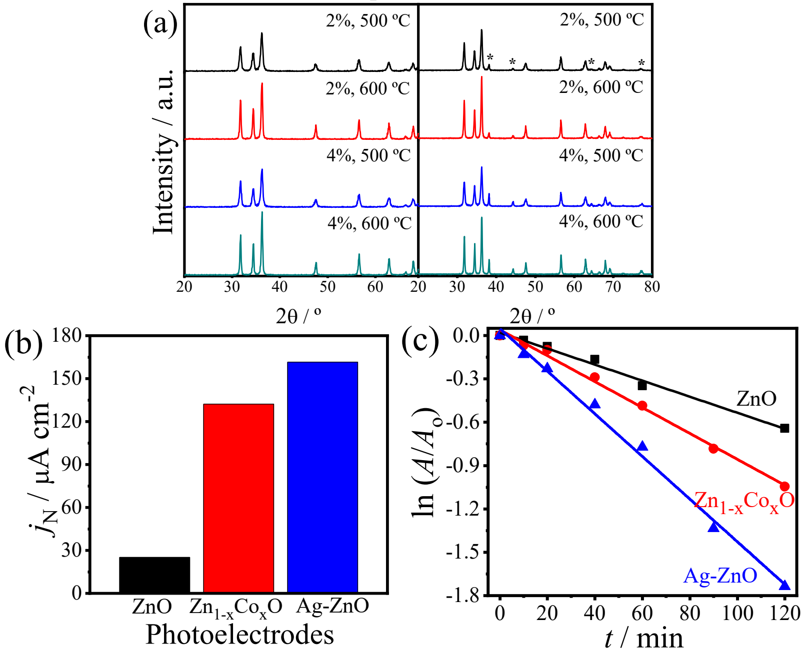

Fig. 1 – (a) X-ray diffraction for $Zn_{1-x}Co_xO$ and Ag-ZnO samples, (b) current density and (c), photoelectrocatalytic responses for the MB discoloration reaction, for ZnO, $Zn_{1-x}Co_xO$ and Ag-ZnO photoelectrodes (E_{app} = +1.0 V, UV light). Electrolyte: 0.1 mol L^{-1} Na_2SO_4 solution.

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Highly stable bifunction HOR catalysts for membraneless Alkaline Fuel Cell

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Fuel cells are one of the most mature technology for green energy, specifically the proton exchanged membrane fuel cell (PEMFC) that depends mostly on the use of expensive platinum group metals (PGMs) [1]. Recently, alkaline exchanged membrane fuel cell (AEMFC) have been received a major attention for advanced and low-cost catalysts. Although there are efficient non-PGM catalysts for alkaline -oxygen reduction reaction (ORR), Pt/C still has the highest performance for alkaline -hydrogen oxidation reaction (HOR) [2]. Beside their cost, the biggest disadvantage of Pt/C and other monometallic PGMs is their drastic degradation in electrochemical surface area and performance at high pH. Several works of Chatenet *et al.* on accelerated stress test (AST) combined with identical location transmission electron microscopy (IL-TEM) showed that Pt assists the local carbon corrosion, leading to CO_2/carbonates formation, and particles detachment [3]. In contrast, bimetallic or bifunction catalysts showed better durability compared to monometallic ones, such as Pd-Pt [4] and Pd-Ni [5] alloy nanoparticles. Bifunction catalyst can also enhance the sluggish kinetic of monometallic PGM in alkaline -HOR, according to the metal-metal oxide theory of Markovic *et al.* [6]. Following this insight, GenCell Energy, Israel patented two compositions of Pd-Pt and Pd-Ni on high surface activated carbon to be used in caustic solution (up to 6.6M KOH in a membraneless alkaline fuel cell set up). In this work, the stable performance of those catalysts was evaluated in 0.1M KOH before and after Ar-AST (150 cycles and 1000 cycles, 0.1 V_{RHE} - 1.2 V_{RHE}, 100 mV/s scan rate). Their physical and chemical properties before and after AST were evaluated by IL-TEM, XRD, XPS and Raman spectroscopy. As expected, both Pd-Pt and Pd-Ni showed better stability compared to monometallic Pt/C and Pd/C (ETEK). Figure 1 presents very little loss of nanoparticles and reasonable agglomeration of Pd-Ni and Pd-Pt catalysts after Ar-AST 150 cycles.

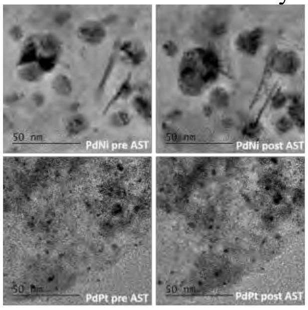

Figure 1: IL-TEM of pre and post Ar-AST 150 cycles (0.1 V_{RHE} -1.2 V_{RHE}, 100 mV/s scan rate).

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Electroactivity of Selected Rare Earth Elements in Dicyanamide-Based Room Temperature Ionic Liquids

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In this work the electrochemical behavior of some selected rare earth (RRE) was evaluated by cyclic voltammetry (VC) in dicyanamide - based room temperature ionic liquid [1].

The studied elements (yttrium, lanthanum, neodymium and samarium) show an electrochemical response that is dependent both on their reduction electrochemical process (in a single step or in a two consecutive steps) and on their associated oxidation process.

From these results and in account of the voltammetric behavior, it is possible to conclude that the studied REE are reduced and oxidized at very similar processes as in aqueous media, molecular solvents and high temperature molten salts [1-9].

The obtained results of the comparison of the electrochemical behavior of the studied REE allow us to propose the possibility of selectively identifying the studied REE in the context of their differing electrochemical responses.

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SILAR Process Deposition: An Interesting Methodology to Obtain $Fe_2V_4O_{13}$ Film With Good Photoelectrochemical Properties

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The research and development of new materials with catalytic properties is essential due to the growing industrial development, energy crisis and environmental problems. Vanadates represent a very important class among the commonly used catalytic and photocatalytic materials. For instance, iron vanadates receive attention due to their distinguished properties. The $Fe_2V_4O_{13}$ (n-type) semiconductor stands out due to its low band gap energy, high chemical stability, low cost and ecologically friendly, which makes it promise for use in electrochemical sensors[1], cathode in batteries[2] and photoelectrochemical water oxidation[3]. In this context, the research to materials with better photoelectrocatalytic performances achieves in the SILAR process a way to improve the properties of the $Fe_2V_4O_{13}$. The present work aims to evaluate the electrochemical properties of $Fe_2V_4O_{13}$ film obtained by the SILAR process with 5 layers. The physicochemical film characterization was performed through X-ray diffraction (XRD), Raman spectroscopy, diffuse reflectance and scanning electron microscopy (SEM) techniques, as well as electrochemical characterization through linear sweep voltammetry (LSV) curves, chronoamperometry and electrochemical impedance spectroscopy (EIS) techniques in to the dark and using visible light irradiation (Blue Laser (FA02)). From the XRD and Raman techniques, it was possible to verify the formation of the $Fe_2V_4O_{13}$ monoclinic crystalline structure. By diffuse reflectance spectroscopy results it was observed 1.71 eV band gap energy. The SEM images show that the average particle size was close to 0.08 µm forming a layer of approximately 4.5 µm on the glass substrate (SnO2:F). Regarding the electrochemical characterization the film presented a high current density under the incidence of light (Fig.1). During the anodic scan under the chopped light condition the behavior of n-type semiconductor film was verified. The transient time was also determined using chronoamperometry (+1.0 V *vs.* Ag/AgCl). The observed low transient time, 10.3 seconds, can be associated with the favorable electrochemical properties of the semiconductor, making it difficult to recombine the photo-generated charge carriers (e^-/h^+). The Mott–Schottky plots leads us to estimate the semiconductor flat band potential approximately +1.06 V *vs.* RHE (Fig. 2). This result agrees with the onset potential observed in the LSV curves under irradiation. This work was possible to determine electrochemical properties for $Fe_2V_4O_{13}$ and based on the results it becomes possible to use this material in future in advanced oxidative processes.

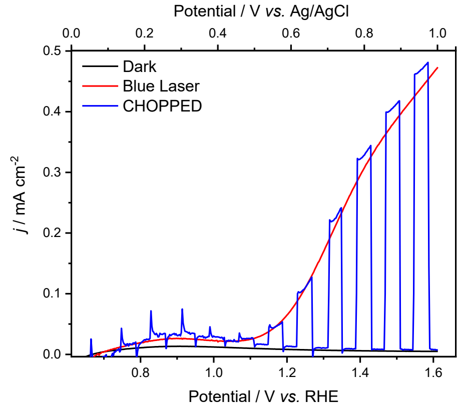

Fig. 1 – Linear sweep voltammetry for FTO/$Fe_2V_4O_{13}$ electrode in 0.1 mol L^{-1} Na_2SO_4 solution, v = 10.0 mV s^{-1}.

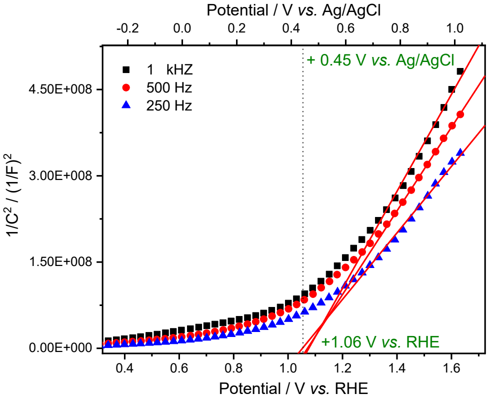

Fig. 2 – Mott–Schottky plots for $Fe_2V_4O_{13}$ collected at a frequency of 1, 0.5 and 0.25 kHz in 0.1 mol L^{-1} Na_2SO_4 solution.

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The birth of an electrochemical garden

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The far-from-equilibrium precipitation reaction of chemical gardens can lead to the formation of biomimetic and complex structures providing a new route for the rational architectural design of functional materials[1].

Inspired by recent developments in the field of chemical gardens[2], we put forward a new scientific question: "Is it possible to create an electrochemical garden?". By implementing state-of-the-art electrochemical techniques and using an otherwise destructive phenomenon, that of metal corrosion, we sculpture self-organized structures on a zinc disc-electrode surface by a mechanism similar to that of chemical gardens. A deeper search in the formation mechanism reveals that ion-selective membranes are the driving force for the growth of an electrochemical garden. At last, electrochemical instabilities, introduced under proper conditions, result in the emergence of current oscillations in the region where electrochemical gardens were discovered. Current oscillations sculpture the electrode surface with a variety of self-organized precipitation structures[3].

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Electrochemical impedance spectroscopy detection of norfloxacin at a polyamic acid modified screen printed carbon electrode.

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Electrochemical sensors have been used in a number of fields such as industry, medicine and agriculture due to their robustness as a sensitive, cost effective and rapid form of molecular detection (Jacobs M, et al., 2013). Electrochemical sensors are devices that change electrochemical information into an analytically signal that is useful. They offer advantages of low detection limits, a wide linear response range as well as good stability and reproducibility. Detection of environmental contaminants using electrochemical methods have advantages of being reliable, fast, portable that can be used for in field analysis to detect environmental pollutants including antibiotic residues (Munteanu FD, et al 2018; Faridbod F, et al., 2011). Norfloxacin is an antibiotic that is usually used to treat complicated urinary tract infection. It has been reported that this antibiotic has been detected in various sources such as surface water, sea water, groundwater and drinking water (Chen, M and Chu, W. 2012). There has been work reported on the detection of norfloxacin (NOR) using electrochemical techniques such as square wave voltammetry (SWV), cyclic voltammetry (CV) and differential pulse voltammetry (DPV). This work reports on the detection of NOR by electrochemical impedance spectroscopy (EIS) in aqueous systems as there is not a lot of work reported on the detection of norfloxacin by EIS. EIS can be used as an analytical tool to measure changes in the electrical properties of the sensor under various analyte concentrations. This electrochemical technique has been extensively utilised for detection of a number of chemical and biological targets in terms of electrochemical change of the electrodes surface (Muñoz J, et al., 2017) EIS have unique advantages compared to CV, SWV and DPV such as ease of signal quantification, ability to separate the surface binding events from the solution and it is also more sensitive compared to the other electrochemical techniques (Chen Z, et al., 2011). This work reports on two different electrochemical detection methods, square wave voltammetry and electrochemical impedance spectroscopy that can be used for detection of norfloxacin in aqueous systems. In this work NOR will be detected by square wave voltammetry and electrochemical impedance at a screen print electrode modified with polyamic acid in 0.1 M pH 7.4 PBS.

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Photoelectrochemical Properties of ITO/MOF 235 Electrode

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The Metal-Organic Frameworks (MOF) is a new class of materials that has had the attention of researchers in the last years. They are structurally based on the presence of a metal ion or clusters linked by an organic ligand in a highly ordered structure, giving rise to materials with pronounced properties [1]. Its main characteristics are its versatility and in its excellent physical-chemical properties, such as a high adsorption capacity, gas storage and catalytic activity and semiconductor behavior[1,2]. MOF 235 stands out among the thousands of different types of MOFs since orange crystals are formed in an octahedral structure and each trivalent iron atom is organized in a network by the organic terephthalic acid ligand[2]. In this study, MOF 235 was easily obtained by the solvothermal method, and its photoelectrochemical properties were investigated by obtaining photoelectrodes by the drop-casting method on conductive ITO glass using different amount of layers (5, 10 and 15). The solid sample was characterized by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) and diffuse reflectance. Regarding electrochemical characterization cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS) techniques were performed. The DRX and FTIR results reveal the formation of MOF 235 by the peaks and bands characteristic of its structure[2]. Based on the diffuse reflectance results the band gap energy was determined 2.0 eV, (Fig. 1-a). The results of CV and chronoamperometry (Fig. 1-b), indicated excellent photoelectrochemical performance with a high current density under irradiation of blue laser. The influence of layers was evaluated by chronoamperometry (Fig. 1-c). The best performance (10.5 µA cm^{-2}) was obtained with 15-layers and its probably related to a large amount of semiconductor deposited. However, impedance measurements demonstrated the lowest charge transference resistance for 5-layers films (246 Ω) (Fig. 1-d). This work demonstrates that a simple and fast route can be used to obtain MOF 235 with excellent photoelectrochemical properties.

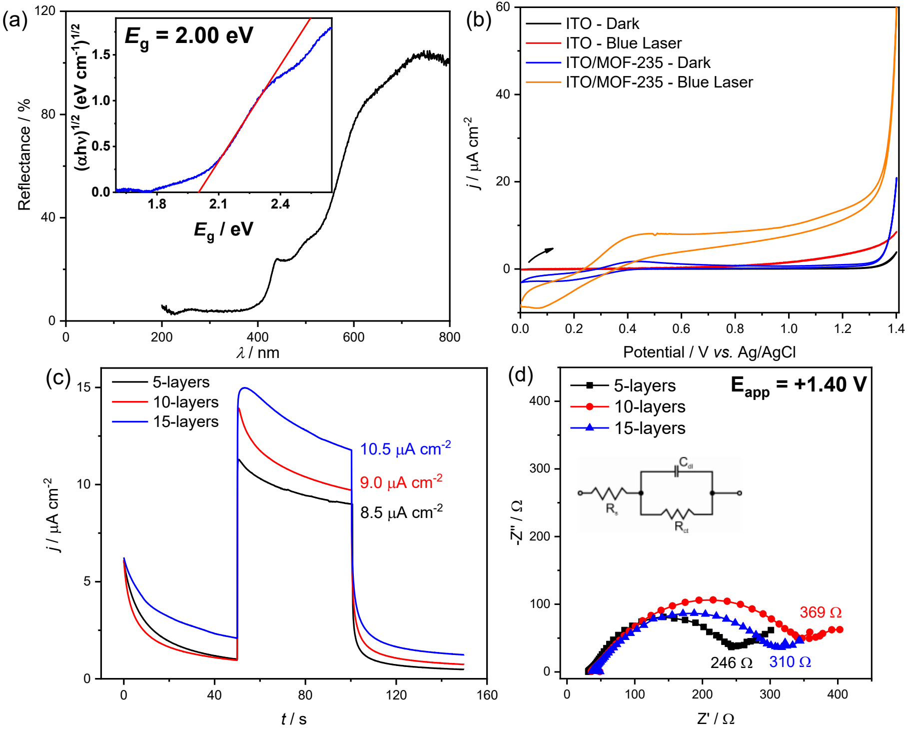

Fig. 1 – (a) – Diffuse reflectance spectra to MOF 235 obtained by solvothermal method, (b) CV for ITO/MOF 235 (5-layers) electrode, (c) chronoamperogram at +1.1 V *vs.* Ag/AgCl with chopped blue laser, and (d) EIS plots for ITO/MOF 235 electrodes. Electrolyte: 0.1 mol L^{-1} Na$_2$SO$_4$ solution.

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Tailored Bipolar Membranes Based on Reduced Graphene Oxide/MoS_2 Hybrid Interfaces for Reduced Crossover in CO_2 Reduction Cells

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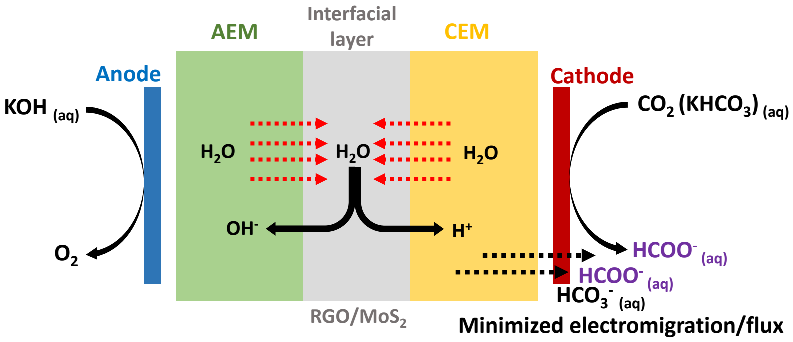
The electrochemical CO_2 reduction (CO_2R) using renewable energy is a promising strategy for the conversion of CO_2 into storable fuels and chemicals while keeping a carbon-neutral energy cycle. Recently, the use of bipolar membranes (BPMs) in CO_2 electrolyzers has emerged as a promising solution to achieve the practical ambitions due to its unique advantage in maintaining a constant pH gradient over the membrane and reducing crossover of ionic and molecular specieces[1,2]. Therefore, elucidation of the crossover dependence on membrane structure, among others, is crucial for advancing the selectivity and efficiency of the process[3]. Herein, a series of BPMs are prepared based on a hybrid interface composed of Reduced Graphene Oxide/MoS_2 catalysts for enhanced water splitting. The cation exchange layer, formed from sulfonated poly(ether ether ketone) (SPEEK) based polymer, is tuned in terms of fixed charge density and water uptake, which is suitably combined with Polybenzimidazole (PBI) based membranes as anion exchange layer. The interface layer is optimized by assessing the impact of the composition and loading of the hybrid catalyst on the electrochemical potential difference over the BPMs. The crossover of anionic products (e.g., formate) through the BPMs - evaluated in terms of the ionic flux, permeability or transport number - is investigated at varying electrolyte concentration (pH) and current density. The ultimate goal is to shed light on the interface structure-property-crossover relationships of BPMs under CO_2 reduction conditions.



Acknowledgment

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Photoelectrochemical Properties of FTO/BiOCl Electrode

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Bismuth oxychloride (BiOCl) is a p-type semiconductor material with a band gap energy of 3.4 eV. This material has been investigated in recent years due to its unique properties, being the packaging layers of -[Cl-Bi-O-Bi-Cl]- which provides the formation of an internal static electric field that facilitates the separation of photogenerated charge carriers, minimizing the recombination processes of the electron/hole pairs. This inherent property leads this material to be applied as electrode materials in photoelectrochemical systems [1,2]. In this work, the FTO/BiOCl electrode was constructed by simple, fast, low cost and efficient SILAR deposition process. The experimental procedure was carried out by immersion of FTO substrate as follows to form one layer: 1) into Bi^{3+} solution ($Bi(NO_3)_{3(aq)}$ 0.1 mol L^{-1} + acetic acid) for 20 seconds; 2) into deionized water for 20 seconds; 3) into Cl^- solution ($KCl_{(aq)}$ 0.1 mol L^{-1}) and finally, 4) into deionized water for 20 seconds. After ten deposited layers, the electrode was dried at 100 °C for 4 hours. The characterization of the BiOCl sample and the FTO/BiOCl electrode was carried out by x-ray diffraction (XRD). Scanning electron microscopy (SEM) and surface area analysis (BET method), were also used. In Fig. 1-a, it is possible to observe the diffractograms of powder sample and FTO/BiOCl film. All the diffracted peaks are in agreeing to the tetragonal structure (P4/nmm and a=b=0.389 nm, c=0.737 nm) (JCPDS 06-0249 standard). The FTO diffracted peaks (SnO_2:F) are also observed. SEM topographic image of the FTO/BiOCl electrode shows a homogeneous micro-aggregate distribution (Fig. 1-b). Besides, the micro-aggregate with the spherical shape is formed up of small particles with an elongated format. The N_2 physisorption analysis indicates a large specific area of 12.5 m^2 g^{-1}. The electrochemical characterization carried out by linear sweep voltammetry (LSV) and chronoamperometry techniques, showed the photoelectrochemical properties of FTO/BiOCl electrode. LSV curves (Fig. 1c) shows the increase in photocurrent density from the scanning potential of +1.0 V to 0 V *vs*. Ag/AgCl under continuous UV light irradiation. This behavior in the *j vs. E* curve is typical of p-type semiconductor material. In the potential scan with the light chopped condition (light on-light off, 5 seconds), the reproducibility of photocurrent is observed. When the light is off the current back to the current value of the dark condition (black line – Fig. 1-c) and when the light is on the current reaches the value of continuous UV light condition (red line – Fig. 1-c). Chronoamperometric measurements, j *vs*. t curves (inset in Fig. 1c), was carried out by applied potential of 0 V *vs*. Ag/AgCl, obtaining a photocurrent density of -18 µA cm^{-2}. Besides, under the light on condition, it is observed the photocurrent stability, wherein in this case, the recombination of charge carriers process may be being suppressed. Then, from the results obtained in this work, the FTO/BiOCl electrode emerges as an interesting material to be applied as a cathode in photoelectrochemical cells.

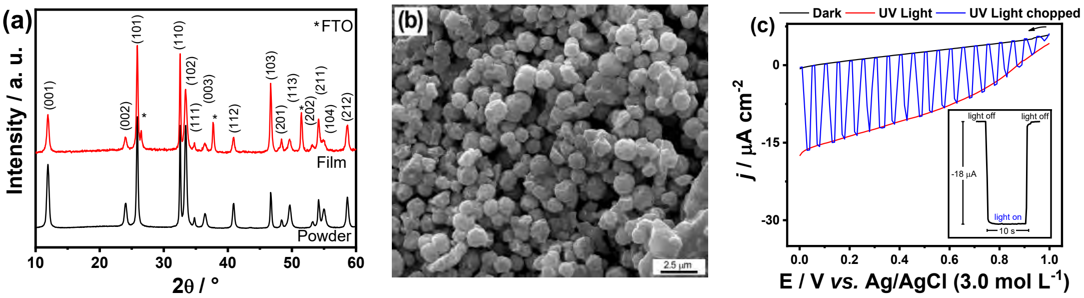

Fig. 1 – (a) X-ray diffractograms of powder and film of BiOCl semiconductor, (b) SEM topographic image of FTO/BiOCl, 12,000× magnification, and (c), LSV of FTO/BiOCl electrode in 0.1 mol L^{-1} KCl solution. Insertion in (c): chronoamperogram under 0 V *vs*. Ag/AgCl in 0.1 mol KCl solution with chopped UV light.

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Phase-Field Modeling of Galvanic Corrosion in Magnesium-Aluminum Joints

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The future design of light-weight vehicles requires a multi-material design approach in which dissimilar alloys are joined together to form a single structure. Aluminum and magnesium alloys are shown to be amongst the best candidate materials for light-weighting purposes due to their superior properties.

However, the joining of Al and Mg is challenging due to galvanic corrosion, a common issue in dissimilar metal joints. A phase-field model to study the galvanic corrosion in Al-Mg joints is presented in this work. The model accounts for the transport of ions in the electrolyte, the electrochemical reactions at the metal-electrolyte interface, and the formation of hydroxide phases on the metal surface (e.g., $Mg(OH)_2$). Two-dimensional simulations are performed to predict the corrosion microstructure, corrosion rate, and galvanic current density in diffusion bonded Al-Mg couples immersed in an electrolyte solution. Galvanic corrosion experiments are conducted for validation. The predictions obtained from the model are compared with those estimated from the experiments. Overall, good agreement is achieved. The corrosion model formulation presented here is intended for later use with microgalvanic corrosion between pure metal and intermetallic phases in complex friction stir welded magnesium-aluminum joint microstructures.

Localized surface modification with SECCM

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During the recent years, scanning electrochemical cell microscopy (SECCM) has mainly been used for studies measuring and mapping local electrochemical processes of electrochemically active materials[1],[2]. For example, SECCM has been used to investigate the heterogeneous electron transfer activity of graphene[3]. Besides, mapping SECCM is also highly suitable for surface patterning[4] and generating nanostructures[5]. Some of the advantages in comparison to the scanning electrochemical microscopy (SECM), are the stable response and the easy fabrication of the SECCM probe. Typically, SECCM experiments are performed with double-barreled nanopipettes with a quasi-reference counter-electrode (QRCE) in both channels, where a thin meniscus droplet at the end of the tip constitutes an electrochemical cell. Since the contact area between the meniscus and the sample surface depends on the tip size, structures possible with nanometer – to micrometer dimensions can be generated.

With this contribution, we present the local modification of carbon-based materials such as graphene or other carbon-based nanomaterials with ruthenium- and cobalt-catalysts. Such catalysts are interesting in molecular-driven photocatalysis. The generated nanostructures are characterized by atomic force microscopy in respect to their structure and size in dependence of the experimental parameter. In addition, TEM analysis will be used. Further investigations will be targeted towards correlated degradation studies for molecular photocatalytic systems.

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Comparative Study of SnS_2 Nanosheets on Micro/Macroscopic Scale

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The two-dimensional semiconductor crystals, such as nanosheets of transitional-metal dichalcogenides (TMDCs) are promising candidates for applications in energy storage/conversion and sensing, due to their tunable structural, electronic and optical properties. However, over these materials, chalcogenides of post-transition metals also show photoactivity in the spectrum of UV-Visible light, such as tin-disulfide (SnS_2).[1] Due to these characteristics, this formerly neglected layered material could also be a great alternative for applications in light-driven catalysis.

It is crucial to understand the photoelectrochemical (PEC) behavior of these crystals to be able to apply them in energy harvesting applications. The reactivity of TMDCs may change extremely with their surface structure (e.g., basal planes and edges, number of layers and defect density).[2] Since SnS_2 nanosheets have not been studied thoroughly in terms of structure-dependent reactivity, the goal of our group was to determine the effects of different surface domains on microscopic scale and compare those to the performance of macroscopic electrodes, in order to enhance its PEC performance.

The micro-scale electrodes were prepared by micromechanical exfoliation from SnS_2 single crystals and were studied with our custom-designed PEC micro-setup. This setup allows us to deposit and maintain microdroplets on the desired part of a nanosheet, with a micro-injection and manipulator system thus to create a 'microelectrochemical cell'. The deposition happens with the help of a microcapillary giving place to the counter- and reference electrodes. The working electrode is the area of the nanosheet, on which the droplet had been deposited. For the macroscopic measurements, bulk SnS_2 crystals were hydrothermally synthesized and exfoliated in formamide.[3] The resultant dispersion was centrifuged at different speeds to obtain two monodisperse fractions in terms of flake thickness and lateral size. The SnS_2 nanosheets prepared by both mechanical and liquid phase exfoliation were characterized with Raman spectroscopy and microscopy techniques (AFM, TEM, SEM). The as-prepared suspensions were used to fabricate the macroscopic electrodes on ITO-coated glass slides. The (photo)electrochemical activity of the nanosheets will be presented with the help of cyclic voltammetry, photovoltammetry and transient measurements (photocurrent transient analysis), focusing the role of the edges and other structural domains.

As a conclusion, the microscopic measurements allow us to better understand how the surface structure affects the (photo)electrochemical behavior of nanosheets, as well as the behavior of macroscopic electrodes fabricated from them. With the help of this approach we will show that the edges of the nanoflakes do not have such a strong negative effect on the photoactivity in case of SnS_2, compared to other TMDCs like MoS2, or $MoSe_2$.[4] Due to this weaker effect, the photoactivity of SnS_2 electrodes could be enhanced more effectively than that of other TMDC electrodes. [5]

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Square wave cathodic adsorptive stripping voltammetry of nanomolar levels of selenium: Application in foodstuffs

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The main goal of this work was the development of a methodology to quantify selenium (Se) in the foodstuffs employing silver solid amalgam electrode modified by a thin and stable mercury film (f-AgSAE) coupled to square-wave cathodic adsorptive stripping voltammetry (SWCASV). Preliminary experiments were realized to verify the suitable analytical signal from SWV experiments using AgSAE in acid (0.1 mol L^{-1} HCl) and basic medium (0.1 mol L^{-1} NaOH plus 0.1 mol L^{-1} KCl), where was observed that the signal analytical (I_p) was strongly influenced by pH of the medium. Besides this, the peak potential (E_p) was dislocated to more cathodic values and half-peak width ($\Delta E_{p1/2}$) have value large with the increase of the pH. After experiments of SWV observed a considerable block of the electrode surface by adsorbed products from redox reaction, providing low repeatability and poor reproducibility. Posteriorly, SWCASV experiments were made using AgSAE and *f*-AgSAE in 0.10 mol L^{-1} HCl solution preconcentration steps (-0.2 V by 30 s), where was observed the presence of a well-defined voltammetric peak under AgSAE and *f*-AgSAE at -0.64 V and -0.50 V, respectively. Besides, the *f*-AgSAE showed higher sensibility and selectivity, due to values of the I_p and $\Delta E_{p1/2}$ present values more favorable than AgSAE.

The preconcentration parameters were evaluated using preconcentration potential from +0.10 to -0.50 V *vs.* Ag/AgCl 3.0 mol L^{-1} in accumulation times from 15 to 90 seconds, and was observed that applying 0.0 V during 90 seconds the I_p presented values around fifty times higher than observed to potential preconcentration more cathodic, and without alteration in the E_p and $\Delta E_{p1/2}$ values. Analytical signals are related to a reaction of irreversible reduction of the Se producing HgSe. Voltammetric parameters were individually evaluated, the pulse amplitude (*a*) was varied in 5 at 50 mV, thus, it observed an increase linear of the I_p up until 50 mV, dislodgment in E_p to less cathodic potential direction, but provoked widening in the voltammetric peak baseline, due to 25 mV was selected. Already, the variation of the pulse potential frequency (*f*) was realized from 10 to 300 s^{-1} observing increase linear of I_p with *f* square root, that is typical reaction was controlled by the diffusion rate. Besides this, the Lovric's Equation enabled the calculation of the number of electrons of the reaction of the surface, according to the relationship between the f and E_p, theses reactions that were 4 electrons, and it made possible the verification of the mechanism reduction of selenium. Thus, 90 s^{-1} was chosen to further experiments, and scan potential increment (ΔEs) was chosen value of -2 mV, due to loss of the peak profile.

Parameter	This work
LR (μmol L^{-1})	0.10 - 8.0
r	0.9989
DL (mol L^{-1})	1.0071×10^{-9} 80.53 ng L^{-1}
QL (mol L^{-1})	3.3570×10^{-9} 268.4 ng L^{-1}
Recovery (%)	101.00
Reproducibility (%)	4.90
Repeatability (%)	1.64

Table 1: Analytical parameters for the determination of Se in pure electrolyte on *f*-AgSAE, where LR is the linearity range, r is the correlation coefficient, DL and QL are detection and quantification limit, respectively.

So, analytical curves were built using standar addition method in a linear range from 0.10 to 8.0 μmol L^{-1}, and the analytical parameters were calculated and are shown in Table 1. The correlation coefficient (r) demonstrated excellent linearity. The detection and quantification limits (DL and QL) presented values like obtained using other electrodic surfaces and spectroscopic techniques. The methodology precision was evaluated by repeatability and reproducibility and indicated suitable values that were below 5.0%. While the accuracy was measured according to recovery curves obtained 101.0%. The coconut water, soy juice, soy milk, apple, orange, potato, spinach, and tomato were previously digested using nitric, perchloric, hydrochloric acid, and after this was made recovery curves and obtained recovery values variated from 101.78 to 170.76 %.

The use of the *f*-AgSAE with SWCASV decreased the waste generation and allowed sensitive, selective, reproductive, and yet quick analysis, is a suitable methodology to the determination of Se in foodstuffs samples.

Comparative Corrosion Studies of TiO_2 Coatings Doped with Metal Ions of Biomedical Importance

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Biomaterials as materials implanted into a living system must fulfill stringent requirements. Nowadays, studies on biomaterials are focused on enhancing their bioactivity and giving them new properties, e.g. antibacterial properties. One of the methods used for preparation of biomaterials with desirable properties is coating their surfaces with functionalized coatings. For example bioactivity may be enhanced by ion doping procedure – the coating is doped with metal ions e.g. calcium and strontium ions. The antibacterial properties may be also achieved by doping procedure – for that purpose silver, copper, zinc or gallium ions are used as antibacterial agent. Unfortunately, every performed functionalization may cause deterioration of other features of biomaterials. Therefore, it is important to control the impact of carried out modifications on other material features, especially corrosion resistance.

The main goal of this study was to apply the sol-gel method for the preparation of protective ceramic coatings of titanium dioxide and their modification by doping of silver, copper, zinc, and gallium ions, that are of antibacterial importance [1-2].

In this study, TiO_2 sol-gel coatings doped with different metal ions were produced on the surface of M30NW biomedical alloy substrates. The titanium tetrabutoxide was used as a precursor of titanium dioxide. In the doping procedure, the nitrates of silver, copper, zinc, and gallium were used as precursors of particular ions. The content of individual ions in the coating was the same and amounted to 5%. The TiO_2-based coatings were calcined at a temperature of 450°C to obtain anatase structure. The effect of each dopant on microstructural and anticorrosion properties of TiO_2-based coatings was investigated.

The morphology, topography and roughness of TiO_2-based coatings were investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The corrosion measurements were carried out in Phosphate Buffered Saline (PBS) solution using electrochemical methods: linear polarization resistance (LPR), potentiodynamic polarization, and electrochemical impedance spectroscopy. Anticorrosion properties of TiO_2-based coatings were specified on the basis of the results of electrochemical tests.

The sol-gel procedure and annealing temperature of 450°C applied in this study allowed the synthesis of crystalline TiO_2 coating with a thickness of ca. 70 nm. Using the sol-gel procedure the TiO_2 coating was successfully functionalized by doping of silver, copper, zinc, and gallium ions. Depending on doped ion the surface morphology of the coating was different. It was found that the addition of copper and gallium ions does not affect surface roughness, while doping with silver and zinc ions increases surface development. The results of corrosion tests in PBS solution confirmed the anticorrosion properties of all TiO_2-based coatings. However, the anticorrosive nature of titanium dioxide coatings doped with ions of antibacterial activity can be ranked as follows: $Cu\_TiO_2 < TiO_2 < Ag\_TiO_2 < Zn\_TiO_2 < Ga\_TiO_2$.

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Predicting Properties of Biocompatible Ionic Liquids and Their Mixtures with Molecular Dynamics

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Ionic liquids (IL) are well-known as candidates for energy storage-and-transformation applications [1]. Herewith, conventional ILs are toxic and harmful to the environment. Biocompatible ILs yield when choline cation is combined with carboxylate anions. Yet, the primary drawback of such ILs is a higher melting point and poor charge transport properties [2]. One way to lower the melting point is to create eutectic mixtures of ILs [3]. The current work demonstrates that molecular dynamics (MD) is a suitable method for predicting properties of possible combinations and compositions of ILs and their mixtures. The solid phases can be obtained by applying Coulombic potential wells to a system of randomly packed ions. Then, the melting points can be determined from a change of slope in the diffusion coefficient *vs.* inverse temperature (Figure 1) during simulated annealing [4]. The presented MD-based method was tested on 13 choline based ILs in work 4 and lately on binary mixtures of ILs for which phase diagrams were predicted (Figure 2).

Biocompatible ILs are possible electrolytes for biomimetic and biomedical applications in smart and soft electroactive polymer actuators. Our recent MD study [5] showed that among other simulated properties, the cation–cation correlation serves as a good predictor of strain difference in such actuators.

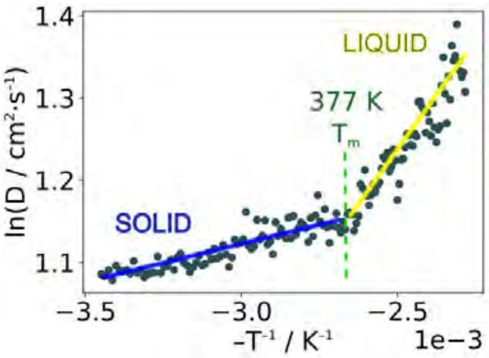

Figure 1: Diffusion coefficient – inverse temperature dependence during simulated annealing.

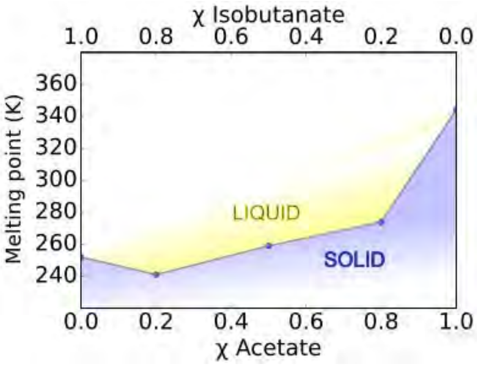

Figure 2: Melting point dependence on anionic molar fraction of mixture (cation is choline).

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Transient and Impedance Response of a Rotating Disk Electrode in a Weak Acid

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Electrochemical current may be influenced by homogeneous reactions adjacent to the electrode. For example, dissociation of a weak acid may enhance the cathodic current through homogeneous supplementation of hydrogen ions. Enhancement is influenced by dissociation rate, diffusion of the weak acid to the electrode, and applied potential. The objective of this work was to model the impedance response and the transient response under a step in potential. The characteristic time constants of the current response are influenced by the homogeneous dissociation of the weak acid.

In previous work,[1] we modeled impedance of a rotating disk electrode adjacent to a nonlinear homogeneous reaction. Numerical results were fit to a modified Gerischer impedance which included the influence of the convection-diffusion and first-order homogeneous kinetics. Recently, Potoskaya and Gicahn[2] derived an analytic expression for the Gerischer impedance when diffusion coefficients are unequal. Their results show that unequal diffusion coefficients influence the Gerischer impedance at low frequency, but the Warburg response for the diffusion of the electroactive species remains unchanged at high frequencies. The observed influence of the homogeneous reaction disappeared for a sufficiently small rate constant.

The objective of the present work was to develop an impedance model and a transient model to investigate the current response of hydrogen reduction on a rotating disk electrode in a weak acid system. Due to the nonlinear homogeneous kinetics of acid dissociation, a numerical finite-difference method was employed to calculate the response for varied acid dissociation rate constants and applied potential. The relationship between the impedance response to oscillating potential and transient response to step potential was investigated. Time constants extracted from the two methods were found to be in good agreement.

Acknowledgement
The support of Medtronic Diabetes (Northridge, CA) is gratefully acknowledged.

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The Effect of the Counter Electrode Material on the Evaluation of Electrocatalysts

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Making accurate measurements of electrocatalytic activity is of paramount importance for the development of new earth-abundant electrocatalysts. In a typical three-electrode setup Pt or Au is often used as the counter electrode material. These metals can dissolve during testing and subsequently deposit on the test electrocatalyst surface, artificially increasing the measured activity. A Nafion membrane is sometimes used to separate the counter electrode from the test electrocatalyst to minimise this, though no work has conclusively proved this to be effective. The work presented here uses X-ray photoelectron spectroscopy, energy-dispersive X-ray analysis, mass spectrometry, and voltammetry to demonstrate the issues with using metallic counter electrodes and the ineffectiveness of Nafion to mitigate this during constant-current testing of electrocatalysts for the hydrogen evolution reaction. It is further shown that a carbon counter electrode can deactivate electrocatalyst surfaces, and that a glass frit should be used to separate the test surface from the counter electrode in these cases.

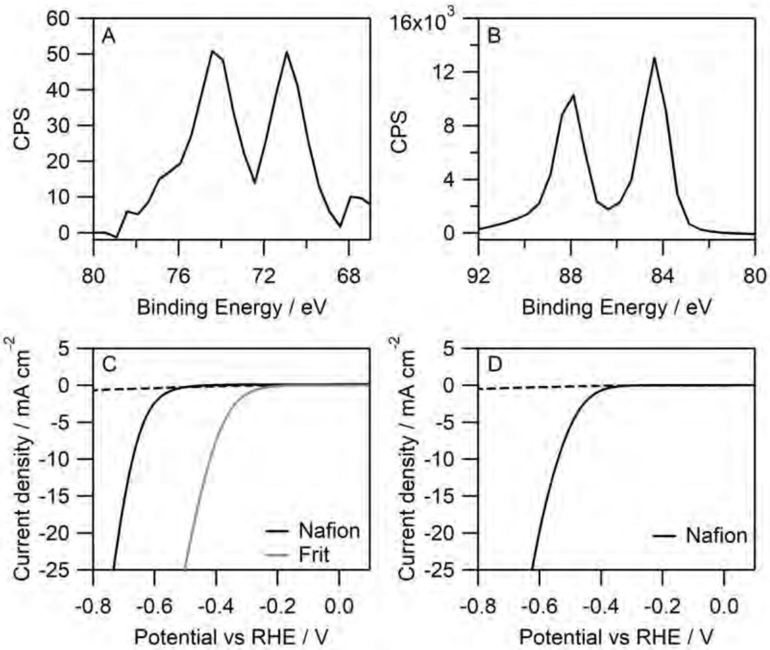

Figure 1: XP spectra of a GC surface after 24 h of HER at –10 mA cm^{-2} in cells containing (A) Pt and (B) Au counter electrodes, with a Nafion membrane separating the counter/reference electrodes from the GC. (C) Voltammograms recorded before (dashed line) and after (solid lines) 24 h of HER at –10 mA cm^{-2} at GC in cells containing a Pt counter electrodes and a Nafion-membrane (black solid line) and glass-frit separator (gray solid line), respectively. (D) Voltammograms recorded before (dashed line) and after (solid line) 24 h of HER at –10 mA cm^{-2} at GC in a cell containing an Au counter electrode and Nafion-membrane separator.

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Photoelectrocatalytic Evaluation of $BiVO_4$/GO nanofibers for application in the photovoltaic cells

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Abstract: The development of materials to monitor and minimize negative impacts on the environment and human health has been widely studied. In this sense, the aim of this work was the development of a high performance device for the , built by electrospinning the $BiVO_4$/GO, obtaining through the technique, nanofibers with high surface area when compared with other techniques of deposition. The BiVO4 band gap value (2.4 eV) and its absorption in the visible region (520 nm), together with the high conductivity of the GO, a p-n heterojunction was formed, thus increasing the efficiency of the device, provided optimum results [1]. Optical and Scanning Electron Microscopes (SEM) were able to morphologically confirm the efficiency of the electrospinning technique in the preparation of the BiVO4/GO nanofibers, showing excellent fiber uniformity, no coalescence and obtaining fibers with diameters between 60 and 96 nm. The photoelectrovoltaics measurements showed a significant improvement in the photogenerated current, using the nanofibers, confirmed by the increase of the peak current and the decrease in the value of the peak potential when compared to other methods of preparation already described in literature [2]. In this way, the data corroborate that the union of the photoelectrocatalytic effect of $BiVO_4$/GO and electro-spinning process have a high potential for applications in the field of renewable energy generation.

Acknowledgement:

CDMF (CEPID/FAPESP) 2013/07296-2, CNPq 159615/2018-6.

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Mathematical Model and Regression Analysis for Electrochemical Impedance Spectroscopy of Continuous Glucose Sensors

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The Continuous Glucose Monitor (CGM) is a device to help patients with diabetes mellitus monitor the blood sugar level in real time and manage hyperglycemia. It includes an enzyme-based glucose sensor implanted under the skin measuring the glucose level in the subcutaneous fluid.

An advanced one-dimensional mathematical model accounting the physics and chemistry of the continuous glucose monitor has been developed.[2,3] The mechanistic model includes the enzymatic reactions, the anomerization equilibrium of α-D-glucose and β-D-glucose, the pH-dependent enzyme activities and the biological buffers. The coupling between the homogeneous reactions and heterogeneous reactions has been described specifically. The physical properties of the sensor and the transport process are also considered. The mathematical model was solved numerically by using the finite-difference method and Newman's BAND algorithm.[4] A systematic parameter investigation has been explored regarding the steady-state profiles and impedance response. The results showed that oxygen and hydrogen peroxide play a key role in the transport-reaction process. Therefore, the electrochemical impedance response is useful for differentiating fault reading caused by oxygen deficiency and enzyme deactivation. It facilitates the understanding of the transport-reaction process and interpretation of the impedance response of sensor under various working conditions, failure mechanism and different sensor designs.

The approach of analyzing the experimental impedance data is shown in the presented work. The process model that accounts for the reactions and physics has been proposed. Regression analysis for the impedance measurement of continuous glucose sensors has been performed based on the measurement model[5,6] and a proposed process model. The measurement model has been used to confirm the consistency of impedance data with the Kramers-Kronig relations. The data flawed by nonstationary behavior and instrument defects is eliminated. The regression of impedance data can extrapolate fitting parameters that have physical meaning and can be correlated with glucose concentration. The study suggests that more information can be extrapolated from impedance response with measurements taken at lower frequencies and lower applied potentials.

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Acknowledgement

The support of Medtronic Diabetes (Northridge, CA) is gratefully acknowledged.

Electrochemical Behavior of Several Metals from Waste Printed Circuit Boards in Acidic Brominated Lixiviants

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Waste printed circuit boards (WPCBs) are the most valuable components of the electrical and electronic equipment wastes, which contain different metals with various ranges of concentrations, including hazardous elements (Pb, As, Cd, Hg), base (Cu, Sn, Zn, Ni, Fe) and precious (Au, Ag, Pd) metals [1]. Recovery of metals from WPCBs is of great importance for both environmental protection and resource re-utilization. The traditional hydrometallurgical approaches for metals recovery from WPCBs use leaching systems that cannot always meet the requirements in the environmental, economic and technic aspects. Therefore, much attention should be paid on developing novel leaching methods that use environmental-friendly and easily recycled lixiviant and oxidant [1].

In the present paper, the dissolution and deposition behaviour of base (Zn, Fe, Ni) and metals precious (Au, Ag) was investigated in an acidic bromine-containing electrolyte that could be used as lixiviant in hydrometallurgical route of metals recovery. The experiments were performed in synthetic electrolytes containing known concentrations of metallic ions and in real solutions resulted from WPCBs leaching from which the more noble metals *i.e.* Au, Ag, Cu, Sn and Pb were removed by electroextraction.

Cyclic voltammetry and polarization measurements were performed in order to characterize the metals dissolution and electrodeposition processes. The influence of metals concentrations and/or solution pH on the electrodeposition was also investigated to determine the optimum working conditions.

The present study is part of a complex research project aiming to elaborate an innovative and pollutants-free hydrometallurgical technology for metals recovery from WPCBs.

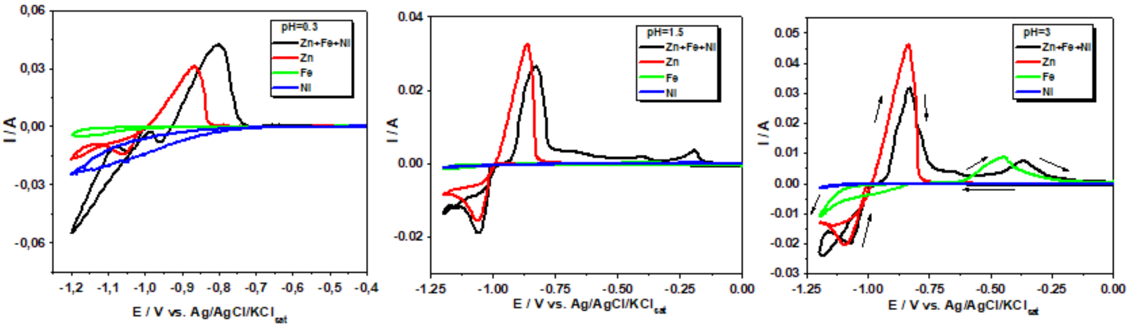

Fig. 1. *Cyclic voltammograms recorded on a glassy carbon electrode from 2 M KBr+0.5 M HBr solutions containing different metal bromides (MBr_2); scan rate 20 mV/s*

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Gold Electrodeposition in Choline Chloride-Oxalic Acid and Choline Chloride-Urea Deep Eutectic Solvents

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Deep Eutectic Solvents (DESs), formed from a quaternary ammonium salt and a hydrogen bond donor, have emerged as alternative media to toxic/corrosive aqueous or organic solvents for electrodeposition processes. These solvents are usually ecologically friendly and conductive enough to be used with no further addition of an electrolyte salt. Speciation is an important factor in metal electrodeposition and owing to the large variety of available DES, the deposit characteristics of a given metal can be extremely different between DES.

The present study concerns the electrodeposition of gold from two differents salts (AuCl and $AuCl_3$) dissolved in two different DES, namely choline chloride - oxalic acid (1: 1) (ChCl-Ox) and the choline chloride – urea (1 : 2) (ChCl-U).

On glassy carbon, the voltammetric features associated with the Au(III)/Au(I) and Au(I)/Au(0) couples are clearly identified. Both are associated with slow kinetics, more particularly in the ChCl-U medium where a very large overpotential is required for Au electrodeposition. By contrast, on platinum, the kinetics of the Au(I)/Au(0) couple is much faster, so that only one cathodic wave associated with a 3 e^- reduction is observed while two anodic peaks corresponding to the 1 e^- oxidation to Au(I) followed by the 2 e^- oxidation to Au(III) are obtained in the ChCl-Ox medium.
The electrochemical data are completed by spectrophotometric measurements and a discussion on the speciation of Au is conducted to rationalise the obtained results.

A Preliminary Investigation into the Microscopic Passivation of new Bio High Entropy Alloys

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In recent years, due to the great advance of scientific and technological research, new alloys are being explored with a different metallurgical concept: at least three basic components and these alloys are called High Entropy Alloys (HEA). In this way it was created the groundwork for a new concept in alloy design by looking after combinations of metals to work "in team" for an advanced material with unique properties.

At the end of the last century, the progress of science led to the rapid development of biomedical materials and the recent development of high entropy alloys (HEA) provides a new perspective for a new generation of biomaterials.

Two new experimental alloys (with the composition presented in Table 1) were obtained by Vacuum Arc Remelting from high purity chemical elements (99.5%) that exhibit extremely low bio-toxicity for the human body (for this reason we named them BioHEA).

Table 1. Chemical composition of the analyzed BioHEA.

	Wt.%					
	Mo	Ta	Ti	Zr	Nb	Fe
BioHEA 1	20.45	32.45	12.67	18.97		15.46
BioHEA 2	17.32	38.95	13.21	17.45	13.07	

The alloys were microstructurally characterized (dendritic morphology, Fig.1 and Fig.2) and microhardness measurements were performed. Both the compositional analysis performed using the dispersive energy probe and the structural characterization by X-ray diffraction revealed the dendritic separation of compounds in the fine dendritic matrix.

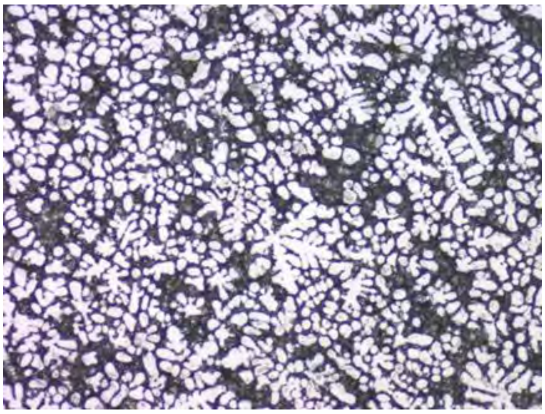

Fig.1. BioHEA 1 microstructure

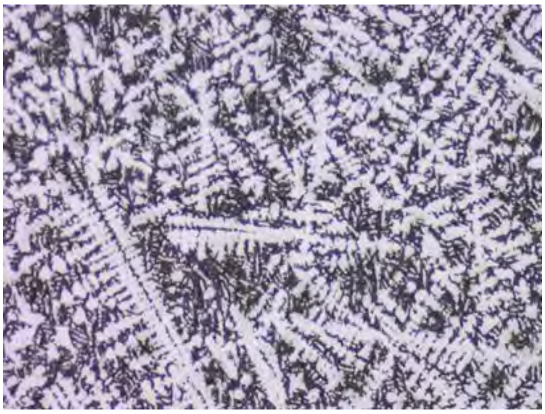

Fig.2. BioHEA 2 microstructure

In order to analyze the passivation process, the electrochemical impedance spectroscopy technique at different potentials was used and the experimental results were compared with those obtained by potentiostatic and potentiodynamic techniques.

The low corrosion rates, low corrosion currents and high polarization resistance attest the good stability of these BioHEA in simulated biological environments.

Influence of the Electrode Substrate (Au, GC, Pt) on the Palladium Electrodeposition in the Choline Chloride-Urea Deep Eutectic Solvent

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Palladium electrodeposition in aqueous media requires potentials close to the decomposition of water, leading to low faradaic yields and embrittlement of electrodeposited palladium. This justifies searching for an alternative electrolyte and the DESs formed from a quaternary ammonium salt and a hydrogen bond donor, have emerged as a judicious choice. These solvents provide relatively large electrochemical potential windows and temperature ranges.

This work reports on the electrodeposition of palladium in the Choline Chloride – Urea (1:2) (ChCl-U) deep eutectic solvent and focuses on the influence of the substrate on the electrochemical behavior of Pd(II).

Curves obtained at a platinum and glassy carbon electrode show two cathodic peaks and two reverse anodic peaks. The first cathodic and anodic responses are linked to the redox reaction of the Pd(II)/Pd(0) couple, while the second cathodic and corresponding anodic waves were attributed to the incorporation and desorption of hydrogen into the deposited palladium.

The overvoltage required for palladium electrodeposition is much higher on glassy carbon than on platinum and associated with a nucleation process.

The gold disc electrode stands out with a different electrochemical behavior signed by the presence of a third cathodic peak which appears long before the two cathodic responses observed on the two previous substrates. No significant overvoltage is required for the deposition of palladium on gold. The most probable explanation of this third response is an under-potential deposition phenomenon of palladium, as observed in an aqueous medium [1]. Rotating disc electrode measurements were performed to obtain more information on these cathodic peaks. Based on these results, the electrochemical behavior of Pd(II) could be separated into four distinct potential zones. In the zone of the most positive potentials the RDE measurements reveal that the intensity corresponding to the first cathodic peak is independent of the rotation rate of the electrode (ω), which indicates a reaction limited by a surface process and confirms our hypothesis of an underpotential deposition in this region.

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A portable electroanalytical procedure with unmodified screen-printed carbon electrode to determine paracetamol in urine and struvite used as organic fertilizers

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Among organic fertilizers, bovine and human urine are natural substance that can replace chemical fertilizers, since they are rich in potassium and nitrogen, and they have compounds that improve plant resistance in terms of health, pests and diseases[1]. The utilization of urine in agriculture can be made both in liquid or solid form, through the precipitation of struvite[2]. Struvite precipitation has been gaining recognition in the agriculture and industrial sector for being an ecological and economical technique that enables the recovery of macronutrients[3,4]. However, some toxic substances present in the urine can contaminate the soil, such as drugs (e.g. paracetamol), once urine is a direct excretion route. Paracetamol in high dosage and continuous indirect consumption can cause gastrointestinal bleeding, exogenous intoxication, hepatitis and liver necrosis, which can lead to death[5]. The present work developed a fast, sensitive, inexpensive and portable procedure for the determination of paracetamol in urine and struvite used as organic fertilizers. In this study, unmodified screen-printed carbon electrodes (SPCE) were used in conjunction with the square wave voltammetry (SWV) technique, employing a drop of solution (40 µL) for analysis.

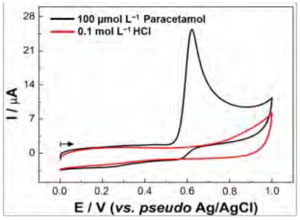

Fig. 1. Cyclic voltamogram of (—) 0.1 mol L^{-1} HCl and (—) 100 µmol L^{-1} paracetamol in 0.1 mol L^{-1} HCl. Potential range applied 0 to 1 V, scan rate 50 mV s^{-1}.

Initially, the voltammetric profile of paracetamol was obtained by cyclic voltammetry (CV), to identify the redox potentials and possible coupled chemical reactions. Fig. 1 represents the cyclic voltammogram of 100 µmol L^{-1} paracetamol in 0.1 mol L^{-1} HCl (pH 1.0). The response obtained for the supporting electrolyte (0.1 mol L^{-1} HCl) indicates that there are no significant background currents, interfering processes or any adjacent reactions in the applied potential range. The pH effect on the voltammetric response of paracetamol was evaluated by CV, in the pH range of 1.0 to 12.0, using HCl, KCl and BR buffers in the presence of 100 µmol L^{-1} of the analyte (Fig. 2). The results demonstrate that 0.1 mol L^{-1} HCl (pH 1.0) was the best support electrolyte.

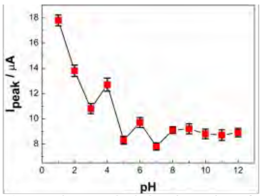

Fig. 2. Peak Current (I_{peak}) dependece with pH for determination of 100 µmol L^{-1} paracetamol in 0.1 mol L^{-1} HCl (pH 1.0), 0.1 mol L^{-1} BR buffer (pH 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, 9.0, 10.0, 11.0 and 12.0) and 0.05 mol L^{-1} KCl (pH 7.0).

The operational parameters of the SWV were optimized by univariate experiments. The optimal values found were: 10 mV (step potential); 40 mV (modulation amplitude) and 15 Hz (frequency). In addition, a SPEC stability study was carried out by application of 50 successive SWV scans. The results indicated that after 25 scans, the SPCE loses the ability to generate reliable responses due to erosion from continuous use of the electrode.

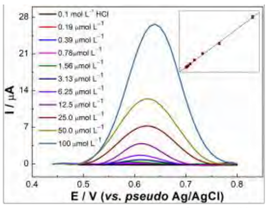

Fig. 3. Square wave voltamograms for the addition of ten solutions of paracetamol (0.19 to 100 µmol L^{-1}) in 0.1 mol L^{-1} HCl.

The analytical curve was constructed in a linear range of 0.19 to 100.0 µmol L^{-1} (Fig. 3). The procedure presented a limit of detection (LOD) and quantification of 0.046 and 0.156 µmol L^{-1}, respectively, and R^2 of 0.998. The determination of paracetamol in struvite and urine samples indicated that the concentration of the drug is below of LOD in both. The recovery tests in different matrices showed values between 92 and 106%, indicating that there is no matrix effect. Based on all of these results, the proposed procedure proved to be effective, simple, fast and a sustainable alternative to promote green chemistry in the determination of paracetamol in urine and struvite.

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A systematic micro-solvation method to estimate solvent effects on adsorption energies

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Electrochemical processes are a promising alternative to convert electricity into chemical energy, thereby contributing to the development of an economy propelled by sustainable energy. The rational improvement of such processes requires in-depth, atomic-scale understanding of the reaction mechanisms and the factors influencing the reaction performance [1], which can be obtained with the help of DFT studies. However, countless electrocatalytic reactions occur in aqueous media where adsorbates and water molecules interact through hydrogen bonds, which are not fully captured by calculations in vacuum. Explicit inclusion of the solvent, in terms of accuracy, is probably the best way to incorporate solvation effects, but its high computational cost makes it unsuitable for mechanistic studies of complex reactions [1, 2]. Conversely, implicit solvation models are practical, and generally inexpensive, however their description of hydrogen bonding is still insufficient in general [3]. Therefore, an alternative approximation is the addition of ad hoc solvation corrections, computed as the difference between the adsorption energies with and without the solvent. In previous DFT-based studies, ad hoc corrections were reported for R-OH adsorbates, either on Cu(111) or Pt(111), with magnitudes from −0.1 to −0.6 eV [4, 5]. Nevertheless, recent works have shown that these corrections may significantly change from one material to the next, introducing errors in the predictions of adsorption energies, reaction pathways, and overpotentials obtained from simulations in vacuum [6].

Here we will introduce a simple and affordable micro-solvation method to estimate the solvation contributions to the adsorption energies [2]. Within this method, an adsorbate-water hydrogen bond occurs when it leads to a more stable energetic state, so that water-adsorbate and water-water interactions are weighed. The method determines the number of water molecules in the first solvation shell of each adsorbate, and the energetic stabilization granted by adsorbate-water hydrogen bonds. The CO_2RR on Cu in aqueous media was used to develop and test the method, and the analysis was extended to Ag, Au and Zn electrodes. Applying the calculated solvation corrections, we find good agreement with experiments in the calculated pathways and onset potentials, with an average error of only 0.07 V. The results obtained on (111) surfaces can be used as ad hoc corrections on other facets of the same metal.

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Formation of Singlet Oxygen in the Oxygen Reduction Reaction in LiTFSI-DMSO in Lithium Oxygen Battery Cathodes

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The formation of singlet oxygen, $^1O_2$, during the O_2 electroreduction reaction on carbon electrodes in lithium bis-(trifluorometilsulfonyl) imide (LiTFSI) in dimetilsulfoxide (DMSO) has been detected “in-operando” by 9,10-dimetil anthracene, (DMA) fluorescence quenching.

The formation of $^1O_2$ during the oxygen electroreduction (ORR) requires Li^+ ions while in the presence of sodium azide, a specific physical quencher of $^1O_2$, the flurescence quenching of DMA is negligible. The addition of Li^+ ions to a superoxide solution in DMSO stabilized by tetrabutylammonium bis-(tri-fluorometilsulfonyl) imide increases the fluorescence decay of DMA, which is a proof of $^1O_2$ formation during superoxide radical anion bimolecular disproportionation:[1]

$$LiO_2^{\cdot} + LiO_2^{\cdot} \rightarrow Li_2O_2 + {}^1O_2$$

The discharge and charge of Li-O_2 batteries under long term operation to deep discharge in repetitive cycles, in the presence of sodium azide in the electrolyte resulted in full charge recovery below 4.3 V vs. Li^+(DMSO) and increased capacity, unlike batteries cycled under similar conditions but in the absence of azide in the electrolyte, where the charge is not recovered. Note that 4.3 V is the stability anodic limit of the solvent DMSO.[2]

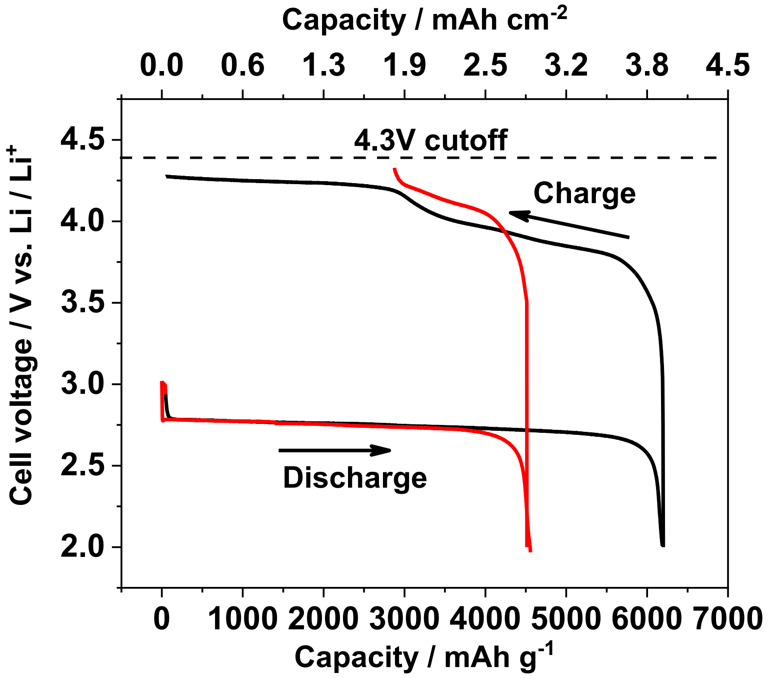

Figure 1. Cell voltage vs. capacity, with azide (black) and without azide (red)

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Voltammetric analysis of kraft black liquor artificial solutions

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Kraft black liquor (BL) is a complex solution mainly composed by inorganic salts used in the pulp cooking process (e.g., NaOH, $NaCO_3$, Na_2SO_4, Na_2S), sugars, hemicellulose, and lignin [1]. Due to its complexity, BL electrochemical behavior is still misunderstood despite the efforts of the scientific community [2–4]. Understanding BL electrochemical processes can be an important advance in the topic of industrial wastewater/environmental electrochemistry. As a result, the electrolysis of this by-product has been significantly explored in the last 5 years and is becoming a promising alternative to process the excess of produced BL [5–7].

Considering that, this work aims to analyze by voltammetric techniques (i.e., by cyclic voltammetry, CV, and linear scan voltammetry, LSV) the behavior of artificial solutions containing the main components of the BL. The initial solution is composed exclusively by KOH + NaOH, being the other inorganic salts gradually added according to the following order: Na_2CO_3 + K_2CO_3, K_2SO_4 + Na_2SO_4, Na_2S. After each addition, CVs and LSVs of this BL artificial solution are recorded using a commercial Pt electrode. Then, lignin is finally added (considering its original concentration in real BL) to the final solution containing all the inorganic salts and the electrochemical behavior of this artificial BL is analyzed. The study is done using acid precipitated lignin and LignoBoost lignin, in order to identify electrochemical differences between them. Finally, the effect of lignin concentration in the voltammetric behavior of the artificial BL is analyzed. All results are critically discussed and compared with the literature to clarify the most important BL electrochemical processes.

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The use of dental amalgam electrode in the folic acid analytical determination: control of the quality breads

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The main goal of this work was the development of an electroanalytical procedure for the determination of folic acid in bread samples using dental amalgam electrode (DAE) and square wave voltammetric (SWV) technique. Preliminary, electronegativity tests were performed in Britton-Robinson (BR) with pH values around to ionization constants of folic acid (pK_a), pH 2.50 and 8.00, which indicated that in the acid medium the redox reaction is more favourable. So, BR and oxalic acid/oxalate buffer in pH 2.50 were individually evaluated and voltammetric responses indicated that in oxalic acid/oxalate buffer the peak potential (E_p) and current intensity (I_p) presented more favourable values, and for this, the pH values of acid/oxalate buffer were changed to 2.00 from 5.00. The voltammetric responses indicated that I_p increased up until the pH 3.00 without loss in voltammetric profile and E_p presented none relationship with the pH, indicating that the protonation is not the step determinant in reaction kinetics. This way, the pH 3.00 were chosen, presenting two well-defined voltammetric peaks, in -0.50 V and -0.84 V *vs* Ag/AgCl 3.0 mol L^{-1}.

SWV parameters were evaluated using pulse amplitude (*a*) from 5 to 50 mV, pulse potential frequency (*f*) from 10 to 250 s^{-1} and scan potential increment (ΔE_s) from 2 to 10 mV. Voltammetric responses indicated that best voltammetric signals were observed using a = 50 mV, f = 250 s^{-1} and ΔE_s = 2 mV. Besides, analysis of E_p and I_p using different *f* values indicated that the electrons transfer occur quickly and following a redox reaction controlled by diffusion rate. Thus, the relationships between E_p and logarithm of *f* values, called as Lovric's Equation, enabled the calculous of electrons number and offers a possible redox mechanism that probably involves the reduction of the group C=N in the main heterocyclic ring, that was previously protonated, following a fast electron transfer with coupled reactions involving an intermediary chemical specie.

Analytical parameters (linear range, linearity coefficient, detection and quantification limits, precision, accuracy and robustness) were evaluated using analytical and recovery curves built using 70 and 250 s^{-1} as *f* parameter, as shown in Table 1. The linearity coefficient (r) value demonstrated good linearity, detection and quantification limits (DL and QL, respectively) were lower than the concentration expected in the bread samples. The precision of methodology was evaluated by repeatability and reproducibility and indicated suitable values, coupled to an adequate recovery efficiency values, indicating that the proposed methodology using DAE and SWV is proper for folic acid determination. All analytical parameters were compared to similar data obtained using the high-performance liquid chromatography with diode array detection (HPLC-DAD), using a precolumn and a column C18, a mobile phase constituted by 0.1 mol L^{-1} of the acetic acid solution and acetonitrile that had a flow rate of 0.6 mL/minute at a temperature of 40°C and an elution gradient with organic phase changing from of the 10 to 24%.

Parameters	***f*** **= 70 s^{-1}**	***f*** **= 250 s^{-1}**	**HPLC-DAD**
LR (μmol L^{-1})	0.1000 – 10.00	0.01000 – 5.000	0.5000 – 5.000
r	0.9955	0.9965	0.9978
DL (mol L^{-1})	$1.202 x 10^{-06}$	$1.726 x 10^{-08}$	$20.299 x 10^{-6}$
QL (mol L^{-1})	$3.641 x 10^{-06}$	$5.2291 x 10^{-08}$	$61.512 x 10^{-6}$
Repeatability (%)	4.73	4.49	-
Reproducibility (%)	5.96	5.07	-
Recovery (%)	93	103	-

Table 1: Analytical parameters for the determination of folic acid in pure electrolyte on DAE, where LR is the linearity range, r is the correlation coefficient, DL and QL are detection and quantification limit, respectively.

The proposed methodology using DAE and SWV was applied in 27 bread samples, which were previously pretreated according to literature reports. The voltammetric data permitted the folic acid quantification in bread samples prepared using different baking temperature and various steam during the process of bread production, permitting the evaluation of the availability of folic acid in commercial bread. So, the proposed methodology presented as an alternative environmentally friendly to the folic acid determination.

Electrodeposition of Germanium Antimony Telluride Microarrays from a Weakly Coordinating, Non-aqueous Electrolyte

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Electrodeposition provides a bottom-up technique compared to conventional coating methods, such as physical vapor deposition (PVD). It is of advantage in the efficient use of the starting material and can be used to plate curved surfaces and even inside of topologically demanding surfaces.

Aqueous electryolytes are commonly used solvent in electrochemical deposition, however, it suffers from narrow deposition potential window which makes water reduction a competing process vs high potential metal reduction/deposition, adding major complexities to experiments. Here we employ an electrolyte system based on tetrabutylammonium chlorometallate metal sources with compatible tetraalkyl halide supporting electrolytes in non-aqueous, weakly coordinating solvents, which provides the ability to deposit alloys with desired structures and properties at high potentials [1, 2].

In this work we report the deposition of germanium antimony telluride (GST) into microstructured TiN arrays from dichloromethane. We present how adjusting the concentrations of the chlorometallates allows control over the composition and also the morphology of the deposits (Figure 1). We also highlight the composition variation of GST deposits in the microarray structures and the design of experiment to minimize the convection effect causing the composition variation.

This work is conducted as part of the ADEPT project funded by EPSRC (EP/N035437/1).

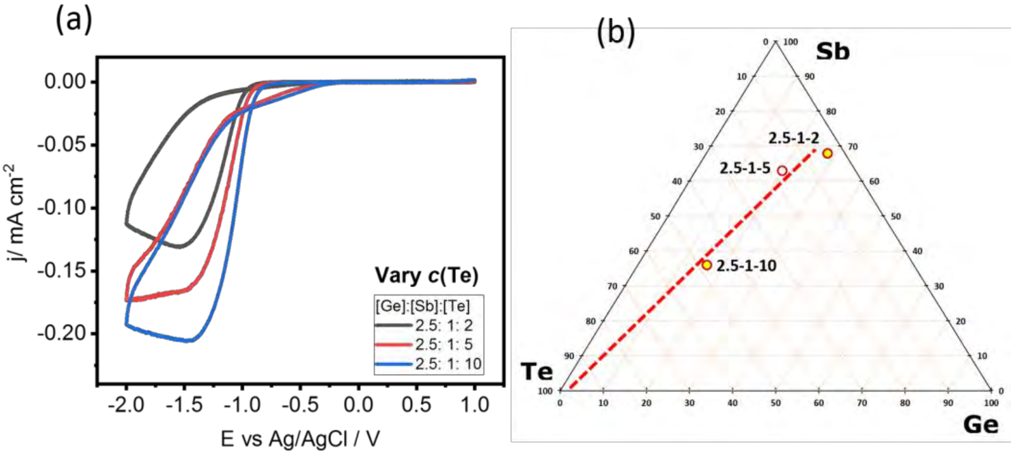

Figure 1: (a) Cyclic voltammetry of 2.5 mM $[NBu^n_4][GeCl_5]$, 1 mM $[NBu^n_4][SbCl_4]$ and a range of $[NBu^n_4]_2[TeCl_6]$ conventrations (black: 2 mM, red: 5 mM and blue: 10 mM) in 0.1 M $[NBu^n_4]Cl$ in CH_2Cl_2 measured at a scan rate of 50 mV s^{-1}. (b) Change in the composition of electrodeposited GST microarrays as a function of the precursor concentration in the plating bath represented as composition triangles.

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Further insights on the kraft black liquor oxidation using rotating ring disk electrode studies

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Understanding the complex mechanism of the electrochemical oxidation of kraft black liquor (BL) is something that requires the combination of different techniques. Conventional electrochemical techniques, such as voltammetry, chronoamperometry, and chronopotentiometry have been already employed in the electrochemical characterization of BL [1-4]. These results allowed the collection of relevant kinetic parameters but do not provide enough information to elaborate a more detailed oxidation mechanism. In order to get additional data on the BL oxidation mechanism, this work involves rotating ring disk electrode (RRDE) studies in real industrial weak BL samples.

The employed RRDE system (Pt ring/Pt disk and Pt ring/Au disk) was used to identify the presence of intermediates and to verify the reversibility of the electrochemical reaction. For that, the Pt ring electrode was maintained at a fixed potential (ranging from 200 mV below OCP to 500 mV above the OCP) while linear scan voltammetry (LSV) was run at the disk. A potential scan rate of 10 mV s^{-1} and rotation of 1200 rpm were applied for all the experiments. The effect of the temperature (25 – 65 ºC) in the electrochemical response was also analyzed. To the best of our knowledge, this is the first black liquor RRDE study that has been reported so far.

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New Pulsed Charge Protocol for Lithium ion Batteries

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Lithium ion-batteries (LIBs) are a widely employed option in the energy storage field for mobile devices (cellphones, electric vehicles, etc.) due to their capacity and power characteristics, and above all their stable cycling. Apart from all the knowledge in the cathode and anode material and electrolyte composition, other important aspect for an optimal operation is the charging protocol. A broad list of charging techniques has been reported[1], but the standard one is a Constant Current-Constant Voltage (CC-CV) protocol.

In this work a new charging methodology is presented. This consist on two steps, firstly a pulsed current period, followed by a pulsed voltage period. Pulsed parameters have the advantage that allows the system to change the diffusional stress in the interface[2]. As innovation, the proposed method applies current and voltage values that oscillate according to a square pulse around a central value without reaching null values.

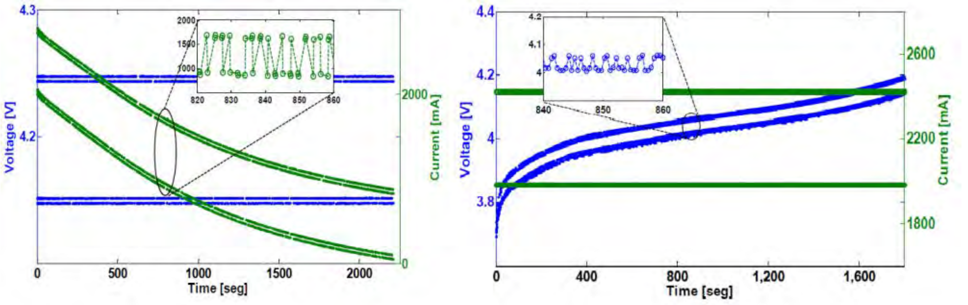

Figure 1: Current (left) and voltage (right) response of a 18650 LIB under voltage pulsed and current pulsed respectively.

The experiments were carried on 18650 LIBs and the protocol was repeated several times to exhibit its impact on the cell capacity over its cycling. The pulse amplitude and frequency of both section was varied to see its impact on the learning curves.

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Graphene quantum dots@Benzoquinone@β-cyclodextrin systems for a dual mode sensing

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Host-Guest inclusion systems have aroused widespread interest, since they play important roles in molecular recognition, particularly in sensor devices. A class of host molecules that has often been used in sensing applications is that of the cyclodextrins, cyclic oligosaccharides that consist of six (α-cyclodextrin), seven (β-cyclodextrin, β-CD), or eight (γ-cyclodextrin) glucose moieties [1]. Depending on the cavity size, cyclodextrins have shown a selective affinity to a wide variety of molecules. For instance, in a previous work, we succeeded to demonstrate the affinity of cyclodextrins for o-toluidine, a toxic water pollutant [2].

Various functional composites based on β-CD have been developed in the Literature. Particularly, Organic-Metal oxides nanocomposites have emerged as an outstanding surface modifier for sensors construction. However, the composite concept can even go beyond this approach by combining electroactive and fluorescent nanomaterials for the creation of a dual-mode sensing device.

Based on this, a novel system based on Graphene Quantum Dots GQDs@Benzoquinone@β-cyclodextrin as a host guest capturing probe was proposed. In this approach, EDC/NHS chemistry was used to covalently immobilize benzoquinone, the electroactive probe, via a cysteamine spacer on graphene quantum dots. Finally, β-cyclodextrin was added via a reductive amination. The optical properties of the synthesized GQDs were studied using UV-vis and PL spectroscopy. Structural and morphological characterizations were examined by the Transmission Electron Microscopy and Fourier-Transform InfraRed spectroscopy. Cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy were performed to investigate the surface modification at each step.

The system was firstly immobilized directly on glassy carbon electrode, then on fluorine tin oxide glass, bare or covered with a thin layer of Titania film, to test the possibility of a dual mode sensing. In fact, the capturing of the target molecule will be accompanied by a simultaneous substantial variation in the benzoquinone electrochemical signal and an evident fluorescence quenching of GQDs.

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Role of the metal center in metal-nitrogen-doped carbons for the electrochemical reduction of carbon dioxide in a continuous flow reactor

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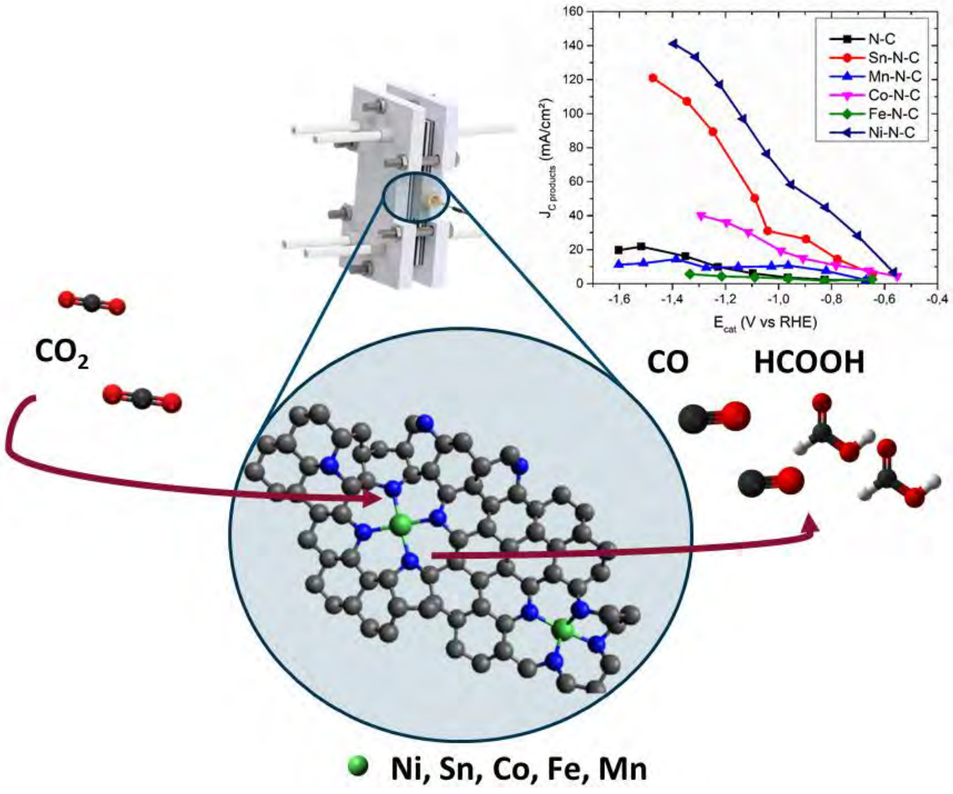
We report the synthesis and operation of various metal-nitrogen-doped carbons for the electrochemical reduction of carbon dioxide to carbon monoxide and/or formic acid as part of a mitigation and adaptation approach to increasing CO_2 atmospheric concentrations. For the first time different transition metals (i.e. Sn, Co, Fe, Mn and Ni) were embedded in nitrogen-doped carbons through an easily up-scalable and tunable method and its performance characterized in a continuous flow reactor at industrially relevant current densities up to 200 mA cm^{-2}. Moreover, changing the embedded transition metal allowed tuning the selectivity towards the desired product. A complete potential-productivity profile was established for CO and/or formic acid yielding better insights into the overall performance of all electrocatalysts. Mn-N-C and Fe-N-C performance was compromised by its high CO* binding energy, while Co-N-C gave way mostly to HER. Ni-N-C and Sn-N-C revealed to be competitive electrocatalysts, being the latter for the first time tested in a flow reactor at high current densities. A productivity of 589 L CO $m^{-2}h^{-1}$ at -1.39 V vs RHE with Ni-N-C and 456 L HCOOH $m^{-2}h^{-1}$ at -1.47 V vs RHE with Sn-N-C was achieved and no signs of degradation were detected after 24 hours of operation at industrially relevant current densities (100 mA cm^{-2}). Stable operation at 200 mA cm^{-2} led to turnover frequencies for the production of carbon products up to 5176 h^{-1}. This unprecedented analysis constitutes an essential step towards the scalability and ultimately towards the economical valorization of CO_2 electrolyzers using metal-containing nitrogen-doped catalysts.



Dental amalgam electrode as a voltammetric tool for triazine-based pesticides determination: application in natural water samples

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The main goal of this work was the use of the dental amalgam electrode (DAE) allied to square wave voltammetry (SWV) in the analytical determination of the ametrine, atrazine and simazine in natural water. The experimental and voltammetric parameters were optimized in Brinton-Robinson buffer at pH 2.5, with a pulse amplitude of 50 mV, pulse frequency of 100 s^{-1}, and scan increment of -2 mV, and consequently, it was presented irreversible well-defined voltammetric peaks at -1.05 V, -0.97 V and -0.99 V *vs* Ag/AgCl 3.0 mol L^{-1} for ametrine, atrazine, and simazine respectively. Additionally, the SWV parameters evaluation indicated the redox reaction of the ametrine and simazine were controlled by diffusion rate, while, the atrazine was controlled by adsorption kinetic. Furthermore, Lovric's Equation enabled the calculation of the number of electrons of these reactions that were 2 electrons, and it made possible the verification of the mechanism of the three triazines, being that the ametrine was the reduction of bond carbon-SCH_3, already, the atrazine reduction of the bond carbon-chloride and the simazine was supposed that occurred atrazine like a mechanism, reducing of the bond of the carbon-chloride bond in the pyridinic ring.

Analytical curves were built for each triazine separately using the standard addition method in a linear range from 0.7500 to 10.00 µmol L^{-1}. All analytical parameters (linear range, determination coefficient, detection and quantification limits, precision and accuracy) were calculations, and are shown in Table 1. The data indicated a suitable linearity and adequate detection and quantification limits, which presented values lower than the maximum limits of residues permitted in natural water by Brazilian Environmental Agency, 100 µg L^{-1} (100 ppb) and near values obtained using the chromatographic techniques and other electrodic surfaces. The methodology precision was evaluated by repeatability and reproducibility experiments producing adequate values, while the accuracy was measured using recovery curves producing recovery values of 100.5, 100.2, 99.6 % to ametrine, atrazine and simazine, respectively.

Parameter	Ametrine	Atrazine	Simazine
LR (µmol L^{-1})	0.7500 – 10.00	0.7500 – 10.00	0.7500 – 10.00
r	0.9989	0.9952	0.9963
DL (mol L^{-1})	1.200×10^{-7} (27.28 µg L^{-1})	1.241×10^{-7} (26.77 µg L^{-1})	1.624×10^{-7} (32.75 µg L^{-1})
QL (mol L^{-1})	3.636×10^{-7} (82.66 µg L^{-1})	3.759×10^{-7} (81.07 µg L^{-1})	4.921×10^{-7} (99.24 µg L^{-1})
Repeatability (%)	2.13	4.25	4.75
Reproducibility (%)	2.58	3.56	2.62
Recovery (%)	100.5	100.2	99.6

Table 1: Analytical parameters for the determination of triazines in pure electrolyte on DAE, where LR is the linearity range, r is the correlation coefficient, S_b is the blank standard from reduction potential values of triazines, DL and QL are detection and quantification limit, respectively.

The proposed methodology was applied in the natural water from Paranaíba River, considering samples characterized by biochemical oxygen demand analysis, that indicated the presence of the 10.8 mg L^{-1}, 11.6 mg L^{-1} and 15.4 mg L^{-1} of total organic compounds considering the sample 1, sample 2 and sample 3, respectively, which are directly related to different levels of organic matter, including wastes from agricultural, industrial and urban activities.

1.0 mL of each sample was mixture with 9.0 mL of BR buffer pH 2.5 in an electrochemical cell and analytical curves and recovery curves were obtained by SWV experiments on the DAE. The inclination of the curves was influenced according to the organic composition, so, the increase of BOD values provided a proportional increase in the slope of the analytical curves, indicating that components interact with the triazines promoting an improvement in the analytical signals. The recovery curves also evaluate the interference of organic and inorganic compounds in the natural water sample, which presented values around to ones obtained in pure electrolyte showing that the sample did not interfere in the voltammetric signals. The methodology proposed was applied in the natural water sample without sample preparation step, showing its robustness. Furthermore, the DAE presented an alternative environmentally friendly to determination of triazines based pesticides.

Correlation between the electrochemical behavior and mechanical properties of Ti-20Zr as a candidate for orthopedic material

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A combination of titanium with zirconium was evaluated because it has been suggested as a candidate for human body implant material and was primarily developed in response to concerns of potential cytotoxicity and adverse tissue reactions caused by vanadium and aluminum in the actually used biomaterial Ti6Al4V.

From all the metallic alloys used in prosthesis, probably the most used one is Ti-6Al-4V alloy. Titanium has poor mechanical strength [1] and when aluminium or vanadium are added to titanium in small quantities, the strength of the alloy is much increased over that of titanium [2]. Therefore, the Ti-6Al-4V alloy achieves considerably higher tensile properties than of pure titanium and this alloy is used in high stress-bearing situations. But Ti-6Al-4V has a potential cytotoxicity and adverse tissue reactions caused by vanadium [3].

Further studies have shown the release of both V and Al ions from the alloy might cause long-term health problems, such as peripheral neuropathy, osteomalacia and Alzheimer diseases.

The microstructure and microhardness were determinate; the tensile strength and electrochemical behavior were evaluated. Titanium is an allotropic element and this mean that exists in more than one crystallographic form. At room temperature has a hexagonal close-packed (hcp) crystal structure, which is referred to as 'alpha' phase. At 883ºC (1621 ºF) this structure transforms to a body-centred cubic (bcc) called 'beta' phase.

The Ti-20Zr alloy, composed of 80% Titanium and 20% Zirconium, (from R&D CS Bucharest, Romania – Research &Development Consulting and Services) was obtained by vacuum melting.

From metallographical images can be observed that the sample has an alpha-beta structure. The microhardness measurements concluded that the alloy formed a hard layer on its surface which greatly improves the wear resistance. The obtained tensile strength can be considered good in relation with other similar implant materials.

The impedance spectra were fitted with two time constants equivalent circuit and the fitting parameters indicate long-term stability of the passive layers in surgical implant conditions.

The results were confirmed by mechanical approach, in terms of two-layer model of the oxide film, consisting of a thin barrier type inner layer and a porous outer layer. The pronounced porous outer layer is expected to facilitate the incorporation of mineral ions and to improve the resistance to electrochemical corrosion over the potential of relevance for human body conditions.

The hardness of Ti-20Zr alloy is 20% higher than that of commercially pure Ti, confirming the alloy's superior mechanical strength.

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Cation Transport in Nickel Hexacyanoferrate Structures: Effect of the Hydrogen Bond Network on the Ionic Mobilities

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Post-lithium metal-ion battery technologies based on Na^+, K^+, Mg^{2+} and Ca^{2+} – ions are attracting more and more attention from the battery community. Recently, the possibility of employing proton-intercalating materials for energy storage applications has been investigated due to the low cost of the materials, environmental friendliness of aqueous solutions and exceedingly high transport rates of protons.[1] Prussian Blue Analogues (PBAs) have been acknowledged as prospective electrode materials for both sodium-ion and potassium-ion batteries due to high diffusivities of Na^+ and K^+ cations, which are achieved due to the presence of large 3d-channels in PBA structures.[2] PBAs can also be considered as suitable materials for proton-intercalation batteries due to the hydrogen bond networks in the structures of hydrated PBAs, which could provide exceptionally high proton transport rates via Grotthuss-type mechanisms. Yet, PBAs exhibit different structures and different phase-transformation patterns[3] depending on the amount of water and intercalated alkali ions in the as-synthesized materials, which calls for the investigation of the effect of the PBA structure type and hydration level on the mobilities of charge-compensating species.

In this work, we focus on comparing potassium-ion and hydroxonium diffusivities in nickel hexacyanoferrate structures. The electrochemical behavior of the PBA cathode materials with the compositions $Ni_{1.5}[Fe(CN)_6]\cdot 6.9H_2O$ and $K_2Ni[Fe(CN)_6]\cdot 1.6H_2O$ was investigated with respect to their charge storage properties in aqueous solutions containing K^+ and H_3O^+ as charge compensating cations. The diffusion coefficients and charge transfer resistances were estimated based on chronoamperometry and electrochemical impedance spectroscopy data. Complementary information on the mechanism of redox transformations of PBA materials in aqueous solutions was obtained based on IR spectroscopy and electrochemical quartz crystal microbalance measurements. Our results indicate that the rates of diffusional transport of cations in nickel hexacyanoferrate structures are strongly dependent on the PBA water content. The presence of a hydrogen bond network in the PBA structure leads to an increase in the proton transport rates and slows down the transport of potassium cations.

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Iron Porphyrin Monolayers Supported on Gold Electrodes: Influence of its Orientation on Electrocatalytic Activity of Oxygen Reduction Reaction

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Iron porphyrins FeP are of high interest in electrocatalysts developing for the oxygen reduction reaction (ORR) in replacement to Pt, which is the best catalyst for ORR but too expensive and ambiently scarce[1,2]. The technological applications require immobilizing FeP on the surface. Many alternatives have been explored to bring FeP to substrate surfaces resulting in different orientations[2,3,4], interaction with the substrate (Van der Walls or covalent bounding), and chemical nature, etc. All these final structures of the FeP on a substrate would affect the ORR performance and this should be taken into account [5].

In this work, we will present the influence on the ORR of the final orientation of 5,10,15,20-Tetrakis(4-phenyl) iron(III) porphyrin (FeTPP) on Au surfaces achieved by immobilization of FeTPP to the surface by two different preparation methods. One method uses *physical vapor deposition* of FeTPP on ultra-high vacuum (UHV) conditions which creates self-assembly monolayers of FeTPP lying flat on the surface (Figure 1.a). A second method consists in *electrografting* of the diazonium salt of the FeTPP in presence of an excess of the radical scavenger, 2,2-diphenyl-1-picrylhydrazil (DPPP) in order to favor monolayer grown, followed by metalation in solution. This second method creates monolayers of FeTPP orientated quasi perpendicular to the surfaces (figure 1.b). Both parallel and perpendicular configurations have been characterized by atomic force microscopy (AFM), scanning tunnel microscopy (STM), X-ray photoelectron spectroscopy (XPS) and electrochemical quartz crystal microbalance (EQCM). Finally, the influence of the orientation and chemical nature of the FeTPP monolayer on the ORR performance has been evaluated by lineal scan voltammetry (LSV) in alkaline solution.

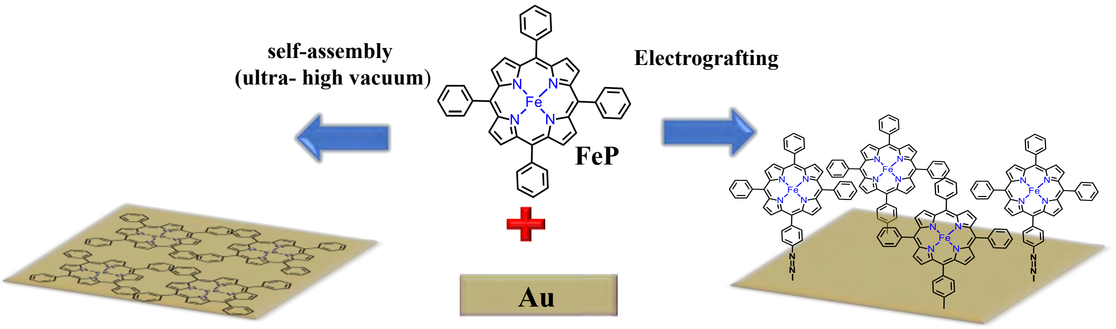

Figure 1. Monolayers of FeTPP obtained on gold surfaces by (a) physical vapor deposition on ultra-high vacuum and (b) electrografting via radical scavenger technique followed by metallization in solution.

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Modeling Self-Similar Periodic Islands in the Oscillatory Electrodissolution of Nickel

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The oscillatory electrodissolution of nickel is one among several reactions utilized as a model-system to study the emergence of oscillations and pattern formation in electrochemical interfaces, in addition to frequently providing experimental proofs for theoretical predictions in synchronization engineering. The reaction was modeled in 1992 by Haim and co-workers[1] and since then the model has been used with great success. Although some numerical studies have been done in this regard, there is still no detailed investigation of the effect of control parameters on the complex dynamics of nickel dissolution. Here, we provide a well-detailed and rigorous analysis of the effect of the external resistance and applied potential by simulating high-resolution phase diagrams based on the calculation of Lyapunov exponents and morphological periods (also known as isospikes[2]) of the time-series. Our findings clearly indicate a strong dependence of the self-similar periodic islands, the so-called "shrimps",[3] with the control parameters. Overall, we observed a low shrimp density in the phase diagrams being completely suppressed in large values of resistance and potential. The shrimp-like structures become gradually elongated with an increase of the control parameters to the point where only diagonally aligned periodic bands intertwined with chaotic domains are present. Interestingly, period-doubling cascades were observed not only on the shrimps but also on the periodic bands. Some of these particularities found in the oscillatory electrodissolution of nickel may be attributed to the exponential dependence of Butler-Volmer kinetics on differential equations.

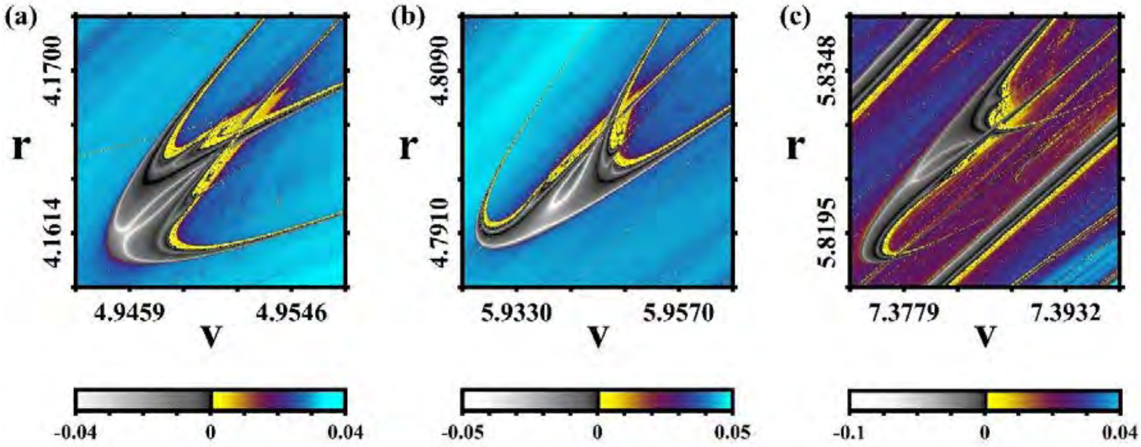

Figure 1 – Lyapunov diagram in the (r, v) control space indicating chaotic and periodic regions for three different ranges of resistance and potential: (a) low, (b) intermediate and (c) high values. Chaos is marked by yellow-cyan scale and periodicity is denoted by white-black one.

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*** A manuscript containing the results described here has been submitted.*

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Probing Speciation and its Applicability to Concentrated Electrolyte Transport Modelling

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Speciation in concentrated electrolytes has been demonstrated to occur due to coordination between solvents, cations, and anions [1]. Interactions between species such as ion pairs impact the transport laws governing diffusion, migration, and convection. To model how composition and potential gradients develop across a concentrated electrolyte, one may need to account for the equilibria between different molecular structures.

The dynamics of ion-pair formation and salt association/dissociation kinetics both can impact the availability of charge-carrying species in an electrolyte. Experimentally, transport and thermodynamic measurements present indicators for ion-pairing, while spectroscopic techniques can further quantify extent of dissociation. Transport phenomena relating to solute and solvent structure, such as Faradaic convection and the excluded-volume effect, can also become dominant in the super-concentrated regime [2]. In very concentrated electrolytes convection can be important because when the salt occupies a large volume fraction of the solution, salt flux across the boundary of a solution drives a bulk solution velocity through overall mass continuity. Faradaic convection can be quantified by combining densitometry with electrochemical measurements.

Newman's application of Onsager–Stefan–Maxwell theory to electrochemical transport considers solute/solute interactions neglected in Nernst–Planck dilute solution theory [3]. The distinction between higher-order species in models may be necessitated by the timescales relevant to bulk transport and ion-pairing dynamics. We will discuss how solute-volume effects and ion-association equilibria influence apparent flux-explicit transport properties such as conductivity, diffusivity and transference number [4].

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Nanostructurated bioactive surface of Ti-Ta alloys for medical devices

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The most commonly used titanium alloy is Ti6Al4V but further studies have shown that the release of both V and Al ions might cause long-term health problems [1,2]. In response to these health problems, new Ti alloys have been developed and among them, titanium-tantalum alloys are expected to become promising candidates for medical applications due firstly to tantalum which is a non-toxic element and secondly due to their better compatibility with bone tissue compared with Ti and Ti6Al4V [3].

The aim of this study is to investigate the influence of tantalum concentration on the behaviour of different bioactive Ti-Ta alloys as biomaterials for medical applications. Three kinds of binary Ti-Ta alloys with 5%,15% and 25% mass tantalum with a surface modification treatment consisting of immersing the samples in hot concentrated NaOH followed by washing with distilled water and dried at 40ºC during 24 hours.

The microstructure of the Ti-Ta alloys was observed by metallographic technique and by scanning tunnelling microscopy (STM).

Were analysed using various roughness parameters such as: arithmetic mean roughness (Ra), maximum height (Ry) and 10-point mean roughness (Rz).

Ti25Ta alloy with lower surface roughness experienced less corrosion when compared to the specimens with higher surface roughness values.

The differences in the hardness and depth of passive layer concerned mostly with bioactive treatment and the concentration of tantalum in the alloy.

Analysis of the impedance spectra was done by fitting these data to the equivalent circuit proposed in Fig.1. The components of the circuit take into account the electrolytic resistance, the resistance and the capacitance of the passive layer, the double layer capacitance and the charge transfer resistance (the model of the surface is presented in Fig.2).

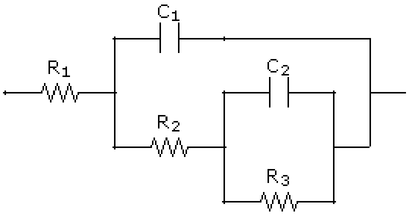

Fig. 1. Equivalent circuit used for fitting the experimental data of EIS

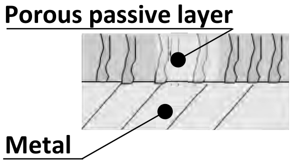

Fig. 2. The model proposed for passive layer formed on the surface of bioactive alloys.

Among studied Ti-Ta alloys, the Ti-25Ta exhibits after chemical treatment, superior properties of the passive film and corrosion behaviour, therefore it appears to be a promising candidate for novel biomaterials. Further experiments are needed to quantify the influence of tantalum content on biocompatibility and cell growth on nanostructurated bioactive Ti-Ta alloys.

Nanostructurated bioactive surface of Ti-Ta alloys for medical devices

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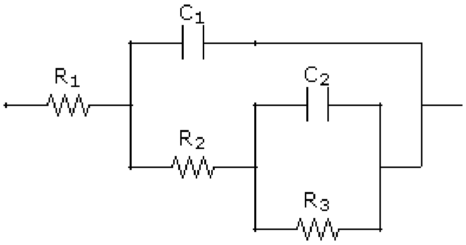

Fig. 3. Equivalent circuit used for fitting the experimental data of EIS

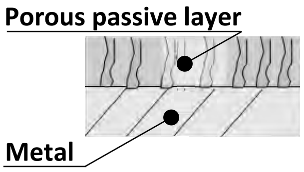

Fig. 4. The model proposed for passive layer formed on the surface of bioactive alloys.

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Increasing the Osseoinduction of Ti6Al7Nb Tibia Implant by Surface Treatment and “in vivo” Application

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Animals such as rats, guinea pigs, rabbits, dogs, sheep, goats, pigs and others with a relatively long life expectancy are suitable for long-term testing of subcutaneous tissues, bones and muscles. Pigs are one of the preferred species as they have organs and osseointegration times similar to humans and this is one of the main reasons why the minipig has been chosen as an experimental animal in our study, mainly focused on analyzing the behavior "in vivo" of a titanium alloy plate Ti6Al7Nb with nanostructured surface, from the point of view of its osseointegration and its toxicity.

A micro-nanocrystalline hydroxyapatite coating on the bioactivated surface has been deposited in two steps: immersion in NaOH solution plus heat treatment and immersion in SBF solution with additional biovitroceramic PAW1 content

.

The importance of the mechanical stability of the implant is evaluated by analyzing the quality of the osseointegration at the bone-implant interface through the analysis of the amount of neoformed bone in direct contact with the implant, able to mechanically fix the implant and the type of bone tissue that is formed.

In this study, the implant was designed so that implantation is simple and as minimally invasive as possible, in the tibia (Fig.1), ensuring optimal bone-implant contact as well as load transmission (bone growth induction).

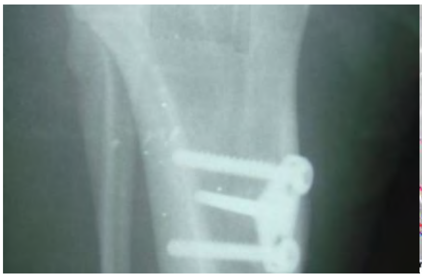

Fig.1. Radiography of the implant

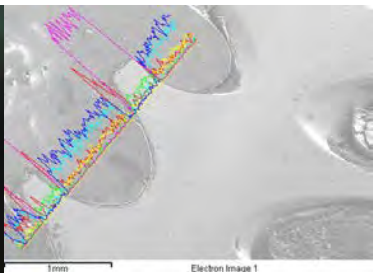

Fig.2. Metal-implant interface analysis

The implantation period has been 6 months and during the healing period the contact between the bone and the implant of each operated pig has been guaranteed, no signs of inflammation have been observed. The toxicity of the implanted metal plate was evaluated by determining the concentration of aluminium by atomic absorption in the different organs of the experimental animals.

Analysis by scanning electron microscope and EDX analyzer of the bone-implant interface of the samples indicates that there is no presence of potentially toxic elements (aluminum) belonging to the implant, results confirmed by electrochemical tests obtained in vitro before implantation.

The study of the bone-implant interface (Fig.2) of the samples from the experimental animals shows that elements belonging to the mineral part of the bone tissue (calcium, phosphorus) have been found. The average of the results obtained from the Ca/P ratio that have been analyzed for each animal allow us to confirm that there is bone growth.

Studies using the atomic absorption spectropy technique indicate that the proportion of aluminium that can affect humans due to the diffusion of this element when wearing an implant is insignificant and cannot be considered harmful compared to daily consumption through food intake or other factors.

Bioenergy generation from glycerol in an MFC using a mixed culture of microorganisms

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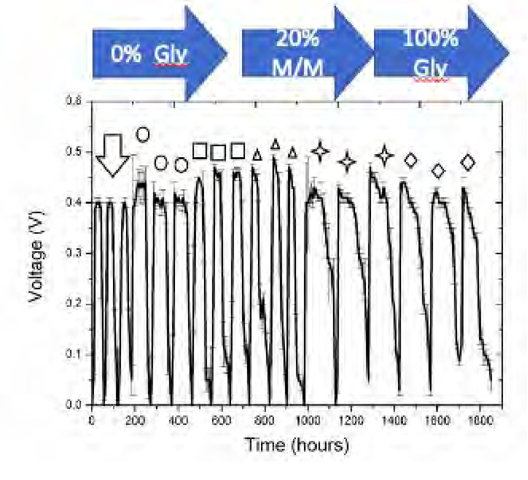
The use of microorganisms immobilized onto the surface of electrodes in MFC devises can be employed to generate efficient electrical energy. In addition, the low environmental impact and variety of fuels and oxidants must be considerate. Recently, we have concentrated our goal to the develop anaerobic degradation of glycerol to produce energy. This may be important to alternative glycerol treatment plus product valorization to overcome the surplus of this fuel. We will report the energy generation of energy employing pure glycerol in an air-breathing MFC with an anaerobic anode compartment (30 mL). The anode (carbon fiber brush - Research Laboratory Shop/China) with 3 x 2 cm was connected with cathode ((HT1400W, ELAT® GDL–BASF) across the external resistance of 1 KU. A mixture culture of microorganisms from a lagoon of Mina Gerais state/Brazil was Inoculated (10 days) in a proper medium [1]. In order to obtain a stable microorganism's films continuous acclimation of glycerol was done by replacement gradually acetate from glycerol (fractions of 20% w/w). We started initially with1.0 g L-1 of acetate until the total replacement of the carbon source for glycerol (1.0 g/L). As can be seen in the figure replacement of acetate for glycerol increases more than 2 times (144 h) the operational cycle of the MFC plus furnishing an increase in the power output (440 mV ± 0.1 or 12.57 mA m-2). These results are higher compared with the ones found in the literature. A good stability of glycerol MFC was obtained in the different feeding cycles investigated. The maximum power density obtained for MFC was 7.7 mW m^{-2} and the maximum current was 25.8 mA m-2. HPLC data showed that the fuel is fast metabolized by the microorganism and the main product at the end of the feeding cycle is propanediol.



Our results showed that glycerol is a suitable and promising substrate for power generation, using a simple two-chamber MFC even at high glycerol concentrations. SEM images showed the formation of the biofilm, predominantly with the rod-shaped. The formation of nanowires was also detected in a large extend.

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Polysulfide reduction in Lithium-Sulfur batteries through the biocatalytic effect of tris(2-carboxyethyl)phosphine hydrochloride (TCEP): A First-Principle study

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Lithium-sulfur batteries are considered as the optimal second-generation commercial battery due to their high theoretical energy density of 2600 Wh kg $^{-1}$ and ~~a high specific~~ a high theoretical specific capacity of 1675 mAh g $^{-1}$, the natural abundance of sulfur~~its natural abundance~~, it's low cost and environmental friendliness [1]. However, Li-S batteries suffer from different problems, such as the insulating nature of sulfur, the change of volume of the active material and the loss of active sulfur material during repeated charge/discharge cycling. Upon lithiation of sulfur, higher-order lithium polysulfides ($Li_2 S_x$ (x =4, 6, and 8)) are generated that are highly soluble in the liquid electrolytes and shuttle across the separator causing low charge/discharge efficiency and corrosion of the lithium anode. This effect produces low utilization of the active material and capacity fades. Another fact that makes Li-S batteries non-~~-~~commerciable until today is the uncontrollable electrodeposition of insulating Li_2S_2 /Li_2S that blocks ion/electron diffusion and decreases the utilization of sulfur [2].~~-~~ To ~~-~~overcome ~~-~~these ~~-~~issues, there ~~are differen t~~are ~~approaches~~different approaches, ~~such~~, ~~as~~such as, ~~incorporation,~~ incorporation of conductive matrices and adsorbent agents in the cathode, optimization of new electrolytes, modification of the separator to reduce the shuttle effect, protection of lithium anode with polymers, among others. ~~But~~However, despite the obtained advances in inhibiting the shuttle effect, ~~it's~~it is worth noting that the nucleation and growth of Li_2S_2/Li_2S is still uncontrolled during the discharge process, which leads to large insoluble Li_2S_2 /Li_2S aggregates.~~-~~ Considering this fact, catalyzing the reduction of long-chain polysulfides to Li_2S_2 /Li_2S and enhancing the reaction kinetics have proven to be valid ways to solve the shuttle effect and improve the rate performance of Li-S batteries. Recently, a series of functional composite interlayers have been systematically investigated to identify the key parameters that determine their role in improving the performance of Li/S batteries. It is well known that trialkyl phosphines have the property of selectively reducing~~e~~ disulfide bonds. Recent~~ly~~ experimental works use the commercially available organophosphorus tris(2- carboxyethyl)phosphine hydrochloride (TCEP) taking advantage of its effect in disrupting disulfide bonds in various proteins [3] to catalyze the cleavage of –S–S– in polysulfides. In the present work, we perform density functional calculations using SIESTA [4] ~~with the aim of understanding~~to understand the specific working principle of TCEP in lithium-sulfur batteries. In this regard, we have performed studies of the interaction of long-~~-~~chain polysulfides with TCEP and studied the TCEP-assisted polysulfide reduction reaction by Nudged elastic band calculations [5]. The reaction steps for TCEP to reduce the polysulfide chains, including the intermediate product of each reduction step (i.e. cleavage site of polysulfides) are elucidated in this work.

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Nano-graphitic templates and hierarchical nanostructures in multi-functional electrocatalysts for CO_2 conversion

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The electrocatalytic reduction of CO_2 is a captivating strategy for the conversion of CO_2 into fuels, to realize a close loop for carbon footprinting. The research has focused on the development of new materials and technology capable of capturing and converting CO_2 into useful products.[1] Among all reduction products, formic acid is particularly attractive for its high volumetric hydrogen density, low toxicity and liquid state, that make it a valuable hydrogen storage vector.

The design of new electrocatalysts that reduce CO_2 in a selective and efficient fashion is a key step for future exploitation of this technology.

Here we present how the combination of different building blocks in a single nanostructure might be a good strategy to achieve a good selectivity in the CO_2 reduction process.

Combining the unique physico-chemical properties of functionalized nanomaterials (such as carbon nanotubes and carbon nanohorns) and nanocrystalline cerium dioxide (CeO_2) we revealed faradaic efficiency for formic acid production as high as 55% at an overpotential as low as 0.02V in acid solutions. These performances have been possible by the formation of partially reduced ceria ($Ce^{4+/3+}O_{2-x}$) responsible of an increased CO_2 adsorption and a more efficient electron transfer at the surface.[2] In the nanocomposite, the carbon nanostructures don't just act as a support, but they counteract the insulating effect of oxide nanoparticles and promote the generation of Ce^{3+} sites. Their elevated surface area and high electrical conductivity guarantee a greater process efficiency.[3] In particular, the nanohorns have a unique conical geometric, where the nano-tips terminals act as "electron collector", increasing the charge mobility.[4]

The interconnection of the various components has been shown to be fundamental for the efficient CO_2 reduction to formic acid with this new metal-free nanocomposite and opens new possibilities in the design of optimized electrocatalytic materials.

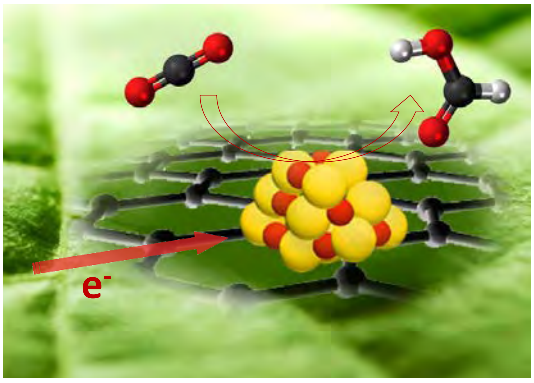

Figure 1. Schematic CO_2 reduction into formic acid on MWCNT@CeO_2

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Reduced Graphene Oxide Fibre Electrodes for Drug Sensing

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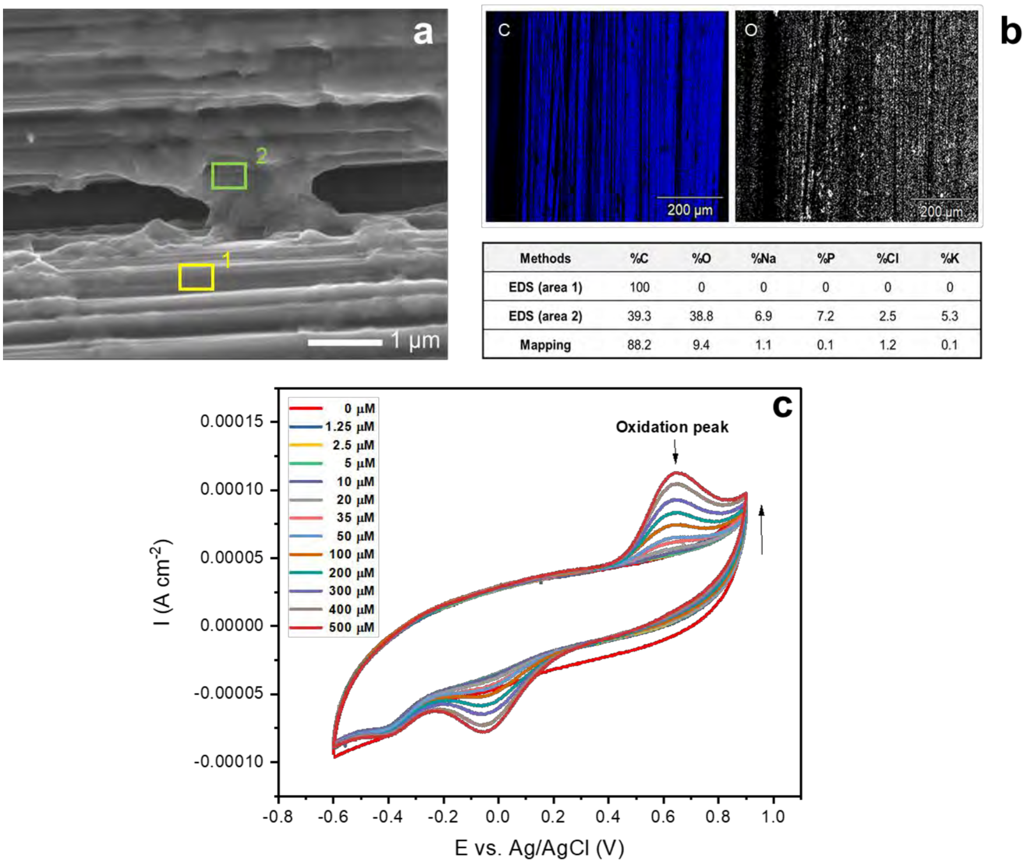
Reduced graphene oxide (rGO) functionalized carbon fibre electrodes and their ability to sense paracetamol (as model drug) in addition to interferents such as ascorbic acid and dopamine were studied. rGO was electrodeposited onto carbon fibre via 2 techniques: potentiostatic deposition and cyclic voltammetry (CV). In CV, the number of CV scans (3 to 20) was varied to study the effect on sensing. rGO-coated on carbon fibres could sense paracetamol at an oxidation peak at 0.62 V (vs Ag/AgCl). The limit of detection for paracetamol, using a carbon fibre coated with rGO using 3 CV cycles, was 10.8 µM (S/N = 3) with a linear range of 0 – 100 µM of paracetamol ($R^2 = 0.9904$). The performance of this sensor with respect to interferents such as ascorbic acid and dopamine, commonly found in blood, was also tested. Increasing the number of CV scans for rGO deposition improved the sensing ability due to an increased electrochemical surface area. The morphology of rGO fibre electrodes was characterised by scanning electron microscopy (SEM) and the presence of rGO on the carbon fibre surface was confirmed by Raman spectroscopic analysis. Further work is underway to sense a range of drug molecules.



Methods	%C	%O	%Na	%P	%Cl	%K
EDS (area 1)	100	0	0	0	0	0
EDS (area 2)	39.3	38.8	6.9	7.2	2.5	5.3
Mapping	88.2	9.4	1.1	0.1	1.2	0.1

Figure 1. Images and sensing data from a carbon fibre coated with rGO using 3 CV cycles: (a) Scanning electron microscope image; (b) Energy-dispersive X-ray spectroscopy (EDS) - mapping images showing chemical composition of Carbon and Oxygen (table gives values for areas not coated (area 1) and coated with rGO (area 2), (c) Cyclic voltammograms (50 mVs^{-1}) with various concentrations of paracetamol (0 – 500 µM) in aqueous 0.1 M PBS solution.

Advanced hybrid electrodes based on polyoxometalate–activated carbon for electrochemical energy storage in Li-ion batteries

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For fast charging and speeding up an electric vehicle, the high power of supercapacitors is needed. Driving a long distance can be realized by the high capacity of a battery. A combination of the advantages of supercapacitors and batteries in one material can bring novel possibilities for electric mobility in the future. Therefore, hybrid materials have attracted much attention in recent years, since they can simultaneously deliver high power and high energy density [1]. Polyoxometalates (POMs), for example, the α-Kegging type: y $H^+\cdot[XM_{12}O_{40}]^{-y}$, are well known as very stable towards oxidation and reduction. These materials show fast and reversible multi-electron transfer reactions [2], and can, therefore, be considered as a promising candidate. In previous experiments, the properties of the POM were optimized for the use in an organic electrolyte by temperature treatment, and the cycling stability of the material improved by 20-times [3].

In this work, activated carbon (AC) was used to prepare POM@AC hybrid material. Due to the absorption properties of the activated carbon, the maximum POM amount was 45 %-wt. The high-temperature optimization of the POM was achieved in one step together with the activated carbon. The combination and optimization of the two materials enables increased cycling stability, as well as a higher capacity with respect to the two single materials (Fig.1). SEM revealed a smaller POM particle size. Therefore the increased capacity can be related to a higher surface of the active material. Further, the hybrid material was characterized by XRD, TGA-DSC, and electrochemically.

Future experiments will focus on increasing the amount of POM on the activated carbon. A higher percentage of POM in the hybrid material, as well as a better distribution of the particles on the surface, can lead to an increase in capacity.

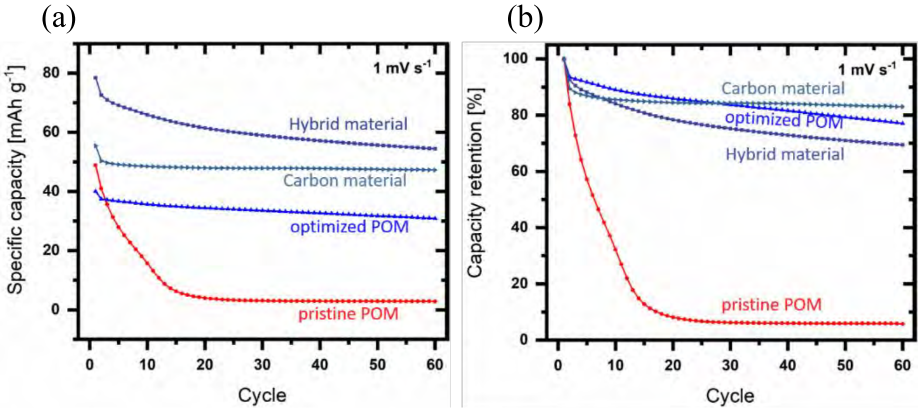

Figure 1: *Comparison of (a) specific capacity and (b) capacity retention of the POM with and without optimized properties, the carbon material, and the carbon-POM-hybrid material. (Measurement was done in LP30 in the potential range 1.4-3.5 V vs. Li/Li$^+$.)*

Acknowledgment
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Developing Machine Learning Algorithms Able To Identify The Tool-Electrode Dipping Depth During Glass Micro-Machining By Spark Assisted Chemical Engraving

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Spark Assisted Chemical Engraving (SACE) is a method for micro-machining glass which utilizes glow discharge electrolysis in alkaline solutions such as sodium or potassium hydroxide [1]. A micro-sized cathode is used as tool-electrode in a two electrode setup. Under high enough cell terminal voltages (typically 25-35V, depending the size of the tool-electrode) glow discharge electrolysis phenomena happens. The electrical discharges happening between the tool and electrolyte trough a gas film surrounding the tool-electrode increase the local temperature to 500-600°C. Bringing the tool-electrode near the workpiece controlled machining by etching of the glass happens.

Controlling of this process requires adequate electrical signals (typically pulses which altering glow discharge electrolysis with regular electrolysis in order to gain a better control over the local temperature) and appropriate tool-electrode motion (combining rotation and relative positioning of the tool to the workpiece). Recently SACE process was commercialized and industrial machines are now available [2]. Even if very high precision micro-parts can be manufactured by SACE (typical surface roughness are well below 1 μm and geometrical accuracy is below typically 5 μm) research is ongoing to enhance further the precision of SACE micro-machining. A major challenge that limits machining precision is the uncontrolled surface *S* that the tool-electrode is in contact with the surrounding electrolyte during the process. This difficulty results from the turbulent nature of glow discharge electrolysis and the motion of the tool-electrode during machining process. A solution would be to adjust the machining parameters (potential and tool motion) in function of the actual surface *S*. This requires a way to measure the dipping depth of the tool-electrode in-line while machining is proceeding. This measurement must be fast as the typical time scale of glow discharge phenomena is a hundred few milliseconds.

In this communication we present the development of machine learning algorithms which are able to identify the dipping depth of the tool during machining within a few milliseconds. The algorithms, based on logistic regression with regularisation using the current signal as input features, are trained on data where the tool electrode is dipped with a known depth into the electrolyte. The algorithms are not only able to identify the dipping depth but can potentially as well give valuable information on the local temperature surrounding the electrode.

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Array Microcell Method (AMCM) for Serial Electroanalysis

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Here we describe a method for electrochemical measurement and synthesis based on the combination of a mobile micropipette and a microelectrode array, which we term the Array MicroCell Method (AMCM) as illustrated by Figure 1. AMCM has the ability to address single electrodes within a microelectrode array (MEA) and provides a simple, low cost format to enable versatile electrochemical measurements. In AMCM a droplet at the tip of a movable micropipette (inner diameter of 50 µm) functions as an electrochemical cell in which the electrode area is defined by a microelectrode of the array. We also report carbon MEAs that are well suited for AMCM and are fabricated from pyrolyzed photoresist films (PPFs). PPF-MEAs with nominal electrode diameters of 5.5 µm are characterized by AMCM, standard macroscale electrochemical methods and finite element modeling. The versatility of AMCM is demonstrated by shape-controlled metal particle electrodepositions, single particle measurements and molecule detection within single cells.

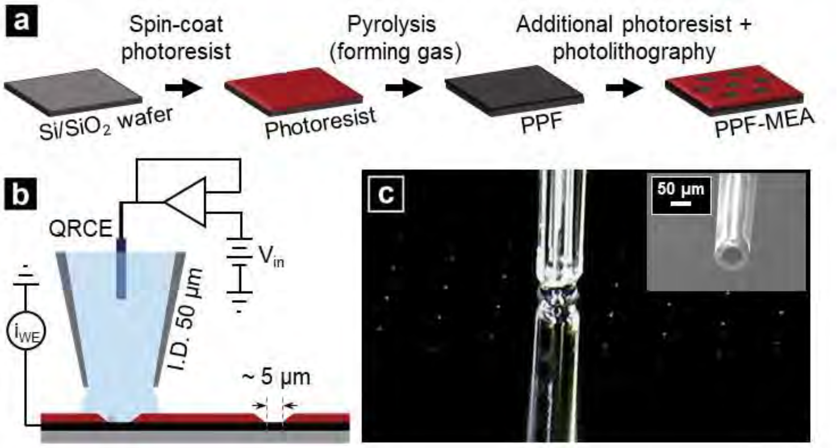

Figure 1. (a) Scheme of pyrolyzed photoresist film-microelectrode array (PPF-MEA) fabrication. (b) AMCM electrochemical measurement setup. (c) Optical image of AMCM, where bright spots are microelectodes 150 µm apart. The inset shows an electron micrograph of a typical pipette used.

Ionic fluxes within porous carbon electrodes operating in aqueous lithium sulphate solution at different pH

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Electrochemical capacitors (ECs) are devices for energy storage and conversion. During EC operation, charge is accumulated at an electrode surface when it is polarized and an electrical double-layer is formed [1]. Because of solely physical interactions between ions and the electrode, ECs are able to deliver energy in a very short time. Processes occurring at the electrode/electrolyte interface seem to be simple – an electrode polarized negatively attracts cations, while an electrode polarized positively attracts anions causing volumetric changes of the electrode [2-4]. To date, ionic fluxes have not been described in detail and it is still an open question how the ions move near the electrode surface, how many of them are attracted to the surface and how the ion exchange proceeds during charge and discharge of the ECs.

In this work, we report on the volumetric changes of microporous carbon electrodes caused by ions adsorption/desorption in aqueous electrolyte – 1 mol L^{-1} Li_2SO_4, measured during in-situ electrochemical dilatometry experiments at different pH values. The results of the preliminary studies are presented in Fig. 1.

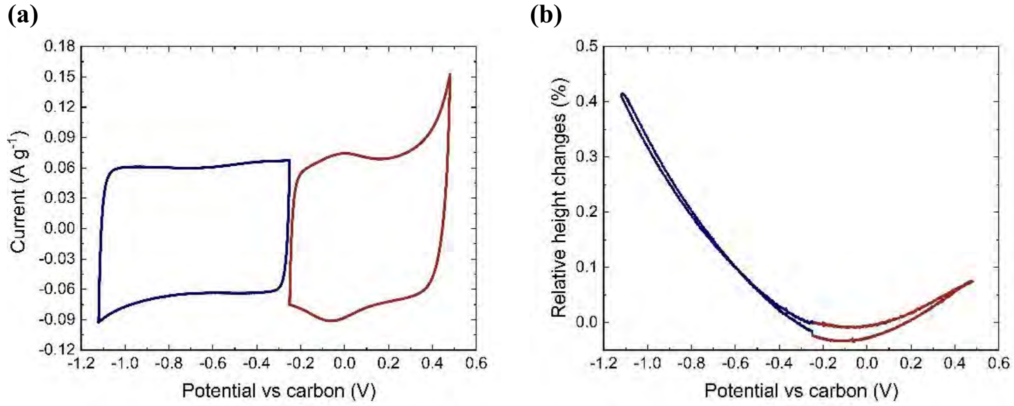

Fig. 1. Cyclic voltammograms (a) and dilatometry curves (b) recorded for the cell operating in 1 mol L^{-1} Li_2SO_4 electrolyte at microporous carbon material (Kuraray YP-80 F) at room temperature

Furthermore, in the case of aqueous electrolytes, pH is a very important parameter because it influences hydrogen and oxygen evolution reaction potentials and, consequently, has an impact on the operating voltage of EC and possible reduction/oxidation reactions of sulphate anion. Moreover, pH may change the hydration energy of ions, thus simplify or hinder a desolvation process. In this context, the paper will bring the insights into composition of the electrolyte at various pH and its impact on the dilatometric response of the polarized electrode.

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Influence of electrolyte CO_2 saturation on aqueous electrochemical capacitor characteristics and long-term performance

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Electrochemical double-layer capacitors (EDLC) operate owing to the physical interactions of electrolyte ions present in the liquid medium with the electrodes. To obtain satisfactory energy output, it is necessary to apply high cell voltage. In the case of exceeding the stability voltage of the electrolyte, the decomposition of the electrolytic medium occurs and the side products are released. In the simplest case of aqueous electrolyte, it is hydrogen at the negative electrode and oxygen at the positive one, as depicted by Pourbaix diagram. At the positive electrode, which is considered to be the limiting one in the system, the material itself can undergo oxidation. It leads to the formation of carbon oxides (most often carbon dioxide). Taking the advantage of Le Chatelier's principle, the foregoing electrolyte saturation with carbon dioxide shifts the equilibrium, thus restrains the destructive electrode oxidation.

$$\text{carbon positive electrode: } 2\ H_2O + C \leftrightarrow CO_2 + 4H^+ + 4e^-$$

The current research focuses on the validation of the above concept. For that purpose, we select the neutral aqueous electrolyte 1 mol L^{-1} $LiNO_3$ and binder-free carbon cloth Kynol 507-20. The electrodes and soaked separator (Whatman Glass fiber A) are placed in a tight electrochemical vessel of ca. 0.5 mL dead volume. Three setups are used:

1. a cell containing the atmospheric air (percentage of CO_2 being 0.4 mbar);
2. a cell with the air being displaced by CO_2 (percentage of CO_2 being 1 bar);
3. a pressurized cell with 3.5 bar CO_2.

The above setups are tested at 1.5 V and 1.8 V to elaborate the CO_2 influence at the sub-boundary conditions and at overexposed voltage, respectively. The electrochemical experimental matrix includes the basic testing and long-term floating. Moreover, the carbon electrodes are physicochemically tested in *post-mortem* mode, for the assessment of their elemental composition, with the special attention to the oxygen content before and after the ageing process (floating experiment). Moreover, the reaction mechanisms will be proposed and discussed.

The initial floating data shows that the CO_2 addition does influence the cell potentials during the test at 1.5 V, what confirms that the reaction equilibria are shifted. The E_0 potentials of the electrodes (i.e. at the discharged state) are presented in Figure 1.

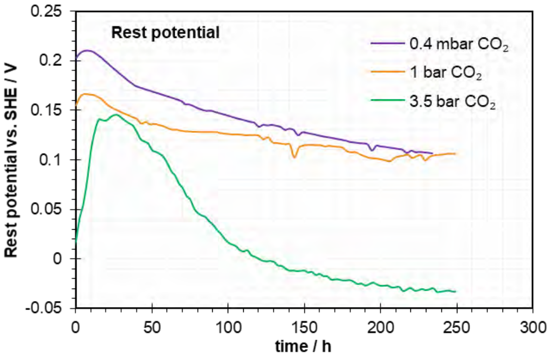

Figure 1. Rest (E_0) potentials of the electrodes during floating experiment at 1.5 V

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Development of electrodes and ion exchange membranes for effective Microbial Desalination Cells

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Fresh water scarcity will arise as one of the major environmental issues in the coming years. Low-energy desalination technologies such as Microbial Desalination Cell (MDC) are needed. Briefly, an MDC consists in a three-chamber electrochemical reactor: an anode and a cathode chambers separated by ionic exchange membranes from a middle chamber (containing saltwater). At the anode, organic matter is oxidized by electroactive bacteria, while at the cathode, reduction processes take place. The redox reaction becomes the driving force for ions removal from the saline chamber by charges compensation. In MIDES project, MDC key components have been studied to increase overall desalination performance.
Carbonous materials (>20), including uni/bidirectional carbon fibers and carbon felts, have been employed as anode materials. Best results, in terms of biofilm formation time (<7days) and current density (>0.3mA/cm^2), were achieved with carbon felt. Besides, electroactive biofilm population differs depending on anode material despite using identical inoculum.

Air-cathodes, based on carbon nanofibers (CNFs) doped with metal nanoparticles (Fe and Co), were developed using electrospinning technique as an alternative to costly and non-regenerative catalysts. Electrochemical tests were performed to evaluate the Oxygen Reduction Reaction (ORR) catalytic activity. CNFs demonstrated suitable ORR performance. CNFs incorporating Fe further enhanced ORR kinetics.

Anionic exchange membranes with low electrical resistance, high permselectivity and anti(bio)fouling properties coatings were developed for MDC application. Their performance was benchmarked with standard membranes, in terms of membrane properties and desalination capacity. Also, their performance over time under MDC operation was studied.

Best performing materials were assembled in MDC for assessing the performance in seawater and brackish water scenarios. Best desalination rates were reached in brackish water, accounting for 2.2 gNaCl/m^2·h, with a 60% salt removal in 72 hours.

Results regarding materials development in MIDES project are likely to be transferrable to other bioelectrochemical systems. Research leading to these results has received funding from EU-Horizon 2020 programme, GA Nº685793 (MIDES project).

On the Development of a Computationally Efficient Model to Predict the Performance of Porous Carbons as Electrode Materials for Electrochemical Capacitors

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Progress in the development of novel energy storage systems is hampered by our lack of understanding of the microscopic mechanisms that determine their performance. The key issue is that phenomena on the atomistic scale have consequences on macroscopic length and timescales. In particular, the effects of ionic confinement and diffusion are crucial for device performance, yet experiments that probe properties related to local structure and diffusion are challenging and difficult to interpret without a parallel modelling approach. In this talk, I will focus on carbon-carbon supercapacitors in which the energy is stored by ion adsorption at the electrode surface. In order to understand fundamentally the macroscopic properties of such systems, it is essential to characterise finely the porous materials used and the structural and dynamic properties of the fluid adsorbed. But, in order to screen materials for energy storage applications, it is necessary to develop computationally efficient methods.

Molecular Dynamics simulations is a very useful tool in the context of energy storage systems as it allows one to get a microscopic picture of the phenomena at play. Here, we focus on concentrated electrolytes in contact with various porous carbons (ordered and disordered) and use molecular dynamics simulations to investigate the structural and dynamic properties of the adsorbed liquid. The concentrated electrolyte is represented using a simple coarse-grained model which allows us to tune its characteristics (e.g. ion size, ion charge) and analyse the effect of such variations on the properties of the system [1]. We then report on the development of a lattice model, to predict quantities of adsorbed ions and capacitances 10,000 times faster than with Molecular Dynamics simulations. While the lattice model is still in a primitive form, it shows some promising results as it is able to reproduce the effects of solvation and pore size observed experimentally [2].

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Characterizing Electrochemical Ligand Removal Au Nanocubes

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Cetyltrimethylammonium bromide (CTAB) is a common organic surfactants employed in seed-mediated synthesis of nanomaterials.[1] Au nanocrystals grown by seed-mediated growth provide an interesting model system to understand nanoscale nucleation and growth, and are also promising technological materials, having found utility as catalysts for energy conversion.[2,3] In some cases, notably catalysis, CTAB ligands adsorbed to the Au surface can prove deleterious to catalytic activity or selectivity.4 In a recent report from our groups, we found that the residual CTAB on Au NCs complicated quantitation by electrochemical imaging.[5]

Methods to remove adsorbed CTAB via chemical treatments have been reported. In particular, thiols containing carboxylic acids,[6] have been explored, with CTAB removal efficiency evaluated by optical spectroscopy such as FT-IR or UV-Vis spectroscopy. Bulk spectroscopic characterization of ligands on three dimensional nanomaterials can prove challenging, however, as monolayer or sub-monolayer quantities can be difficult to detect reliably. Here we demonstrate characterization of CTAB ligands adsorption on Au nanocubes (Au NCs) with a combination of in situ atomic force microscopy and electron microscopy. Highly disperse Au nanocubes (NCs) were utilized as a model system, enabling quantitative comparison of height and width measurement. Force-distance (FD) curves and correlative in situ AFM topography of CTAB adsorbed at Au NCs, compared to SEM measurements provides compelling evidence of the effects of surface cleaning on CTAB adsorbed on the Au NCs.

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Layered and 2D Transition Metal Oxide Materials for Energy Conversion Applications

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Currently, the state-of-the-art materials for the Oxygen Evolution Reaction (OER) and the Oxygen Reduction Rection (ORR), the energy intensive reactions in water electrolysis and fuel cells respectively, stem from the expensive and rare Platinum Group Metals (PGMs). However, major problems remain when using these PGMs for these reactions. For the OER and ORR, most state-of-the-art PGM catalysts exhibit large overpotentials and this value needs to be significantly decreased for electrolysis and fuel cell technologies to become economical.

In general, few layer and 2D-materials exhibit higher surface area and are more conductive than their bulk counterparts therefore hold great promise as next generation materials for the OER and ORR.[1] Hence, as Transition Metal Oxide (TMO) based materials are currently the best performing catalysts for the OER and ORR, it is logical that few layer and 2D TMO materials are likely candidates to emerge as alternative low cost and active catalysts for these electrochemical energy conversion applications.[2] In this work we explore layered and 2D TMO based materials as potential catalysts for these technologies, as we try to create materials with increased active sites, surface areas and conductivity compared to bulk TMO materials.[3]

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Electrocatalytic CO_2 Reduction on CuZnAl-based Oxide Catalysts: Tuning of the H_2/CO Ratio

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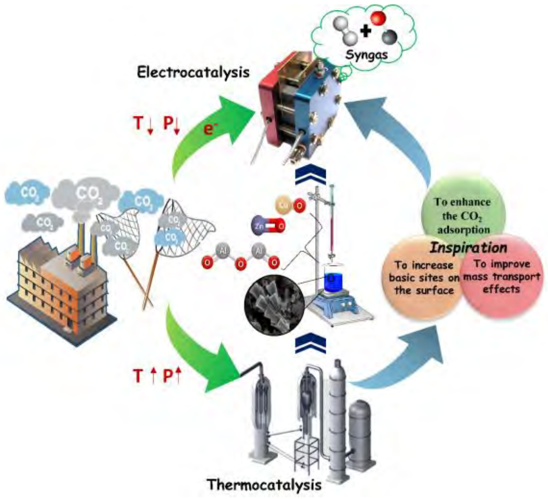
Electrochemical Reduction of CO_2 (ER-CO_2) is a very attractive alternative to tackle Global Warming[1]. Cu-based materials have shown increased yields of hydrocarbon and oxygenate products, while its selectivity towards CO is low[2]. Inspired by the thermocatalytic process, a traditional co-precipitation method was employed to synthesize CuZnAl-based oxide catalysts with a mesoporous structure. This CuZnAl catalyst was tested for the first time for the ER-CO_2 under ambient conditions. The chemical-physical properties of the catalysts were studied by several characterization techniques (e.g. XRD, XPS, BET, SEM, TEM) and electrochemical impedance spectroscopy at different applied-potentials to understand the role of the modification of the catalyst components during operation in the final selectivity and activity. Results revealed that by adding amphoteric metal oxides like ZnO and Al_2O_3 to the CuO-based catalyst contributed to promote CO formation over H_2. XPS measurements on the fresh samples revealed that the ternary CuZnAl catalyst presented a lower percentage (5%) of $Cu^0 + Cu^{1+}$ mixture on the surface than the other catalysts, being mainly constituted by Cu^{+2}. This material reached a Faradaic efficiency towards syngas of almost 95% at -0.89 V vs RHE. Nevertheless, the highest production rate of syngas was obtained at the most negative applied potential (~ 17 µmol h^{-1} cm^{-2} at -1.14 V vs RHE).). A tunable H_2/CO ratio was achieved by applying different potentials, reaching lower values by increasing applied negative potential (CO current density increased). In fact, a syngas with a H_2/CO ratio of ~ 2 was obtained at -0.89 V vs RHE, which is a suitable raw material for further methanol synthesis[3]. The enhanced performance for syngas production of the developed CuZnAl catalyst is demonstrated to be attributed to its surface properties (i.e. alkalinity and the oxidation state on the surface, its lowest diffusional mass transfer resistance, its highest total pore volume and the lowest Cu crystals size among the prepared catalysts.



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Analysis of Lithium Insertion and Deinsertion in Photo-charging Battery System

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The energy conversion of light energy into electricity is one of the most interesting studies to be explored. Light energy as an alternative energy source is utilized for energy conversion devices such as solar cells. Solar cells convert light energy into electrical energy. However, both of the light and electrical energies cannot be stored in their form; thus, it requires the energy conversion from the electrical to the chemical energy using rechargeable batteries. Two steps of energy conversion in the basic solar cell drive the low efficiency of energy converted during device-to-device transfer. The efficient establishment of solar cell technology on a global scale requires an efficient improvement concerning materials and devices to increase the power conversion efficiency. The integration of light-harvesting solar energy with the battery system was expected to drastically improve the energy efficiency.

The photo-electrochemical reaction of lithium-ion insertion and deinsertion has been reported by employing dye-sensitized battery material driven by light irradiation [1]. The light energy generated electron-hole pairs with the holes aiding to the chemical conversion. Nevertheless, energy efficiency and reaction kinetics should be improved by investigating the appropriate anode material for the system. By utilizing the photo-intercalation and photo-deintercalation concept that has been proposed by H. Tributsch in 1983 [2], the light energy can induce the transfer of ions between the electrode and electrolyte when there is a difference of fermi level energy between electrolyte and electrodes in semiconductor materials. Hence, to investigate the basic fundamental studies of the photo-intercalation reaction, active battery materials and semiconductors were utilized in the photochemical cell. A photo-sensitized $LiFePO_4$ has been prepared to be applied as the working electrode, while a silicon p-type semiconductor has a role as the counter electrode in three electrodes battery system. The electrochemical transparent cell was utilized in order to observe the electrical current response from the energy produced by the reaction that takes place under the light irradiation.

The experiment of photo-lithiation was conducted by observing the currents response of the $LiFePO_4$/Si and the potential changes of $LiFePO_4$ vs. Li^+/Li full cell system under light irradiation. There was no electrochemical activation involved in the system. When there was no light irradiation, there was no currents response observed. Meanwhile, there was a distinct current change from 0 mA to ±0.6 mA once the light irradiates the photochemical cell. In order to further analyze the chemical state changes of the electrode materials in the photo-electrochemical system, an experiment was conducted by using X-ray absorption spectroscopy measurement. The experiment was established after the irradiation of light towards the materials. The intense absorption in the near-edge area broadened, and the edge energy was shifted towards lower energy. This trend corresponds with the spectrum change during the electrochemical lithium insertion of the silicon electrode [3]. By this result, we acquired the possibility of advancing the design principles for photo-assisted rechargeable batteries.

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System identification of PEMFCs through EIS and cFRA: a comparative study

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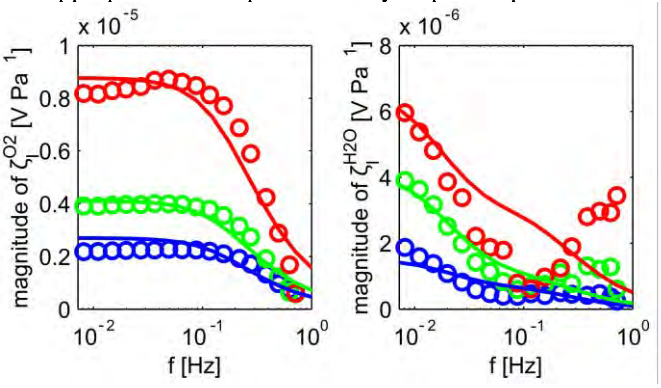
Due to its capability to separate power losses related to different mass transport and kinetic phenomena, electrochemical impedance spectroscopy (EIS) is commonly applied as fault identification tool for polymer electrolyte fuel cells (PEMFCs). However, this is not always the case especially in the lower frequency region of the EIS spectra (< 1 Hz), where the contributions of the gas transport of oxygen and liquid water, water sorption in the Nafion membrane, and adsorption/desorption kinetic steps of the HOR and ORR overlap, becoming practically indistinguishable. In this frequent scenario, the efficacy of EIS as PEMFCs diagnosis tool and its capabilities to estimate key parameters related to the fuel cell performance are inadequate.

Recently, our group has developed a novel frequency response methodology based on the use of periodic concentration as input which aims to overcome the limitations of the EIS at low frequencies [1,2]. The new technique, named concentration-alternating frequency response analysis (cFRA), applies periodic input of oxygen or water at the cathode side of PEMFCs and detects electric responses under galvanostatic or voltastatic conditions, cell potential and current respectively.

In this contribution, an experimental facility capable to produce an input flow with periodic concentration of oxygen or water at different frequencies is presented, and a procedure to measure cFRA spectra is described. Then, by the support of a mathematical model of a PEMFC, the capability of the cFRA to separate the dynamics of gas transport and water sorption in Nafion membrane depending on the kind of concentration input and output is demonstrated (please see the figure below). Finally, the identifiability and estimation of some key PEMFC performance parameters using EIS and cFRA transfer functions have been compared by considering sensitivity and collinearity of the different parameters. Criteria to choose a most appropriate technique to identify a specific parameter are discussed.



$$\zeta_I^{O_2}(\omega)=\frac{\Delta V(\omega)}{\Delta P_{O_2}(\omega)}$$

$$\zeta_I^{H_2O}(\omega)=\frac{\Delta V(\omega)}{\Delta P_{H_2O}(\omega)}$$

Left: cFRA transfer function obtained by periodic oxygen concentration change under galvanostatic conditions. Only dynamics of gas transport in the channel is detected. **Right:** cFRA transfer function obtained by periodic water concentration change under galvanostatic conditions. Only dynamics of water sorption in Nafion is detected.

***Keywords**:* Polymer electrolyte fuel cell, system identification, impedance, frequency response analysis.

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Effect of Oxygen Functionalization of Graphene on the Signal Sensitivity of Dopamine Detection

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We examined the effect of the carboxyl group (–COOH) functionalization at the edges of graphene nanoplatelets (GNPs) for the electrochemical sensing of dopamine (DA) in the presence of ascorbic acid (AA) and uric acid (UA). The –COOH functionalized GNP at the edges (ECG) was prepared by a ball mill method with a high percentage of functional groups (26.40%). For comparison, GNPs with a low percentage of –COOH (2.35%) functionalization was also prepared by the heat treatment of ECG (HECG). Both ECG and HECG dispersions in 2-propanol were used to modify the fluorine-doped tin-oxide electrodes (FTO) by the e-spray method. The ECG/FTO sensor displayed high catalytic activity and sensitivity with the signal separation of DA, AA, and UA, while the HECG/FTO sensor completely suppresses the oxidation signals of AA and UA with a low sensitivity of DA oxidation. This can be ascribed to the varying interaction mechanism of AA^-, DA^+, and UA^- at pH 7.0 with the –COOH groups of ECG and HECG. The differential pulse voltammetry (DPV) signals for the oxidation of DA revealed the detection limits (S/N = 3) of 0.26 and 1.0 μM, respectively, at the ECG/FTO and H-ECG/FTO sensor with the sensitivity of 2.11 and 0.55 $\mu A/cm^2/\mu M$, respectively.

Modeling temperature effects on a graphite Li-ion anode by Kinetic Monte Carlo simulations

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The Li-ion battery is one of the most important devices involved in the change towards a new energetic paradigm, being graphite the most used material as anode due to its high specific capacity, low cost, and low volume expansion, to name a few properties. Li-ion (de)intercalation (from)into graphite involves a series of stable compounds denoted as stages.

Understanding how external variables, such as pressure or temperature, affect batteries is important to improve their operation since they have demonstrated to play a role in several processes, such as changes in the interphase resistance. Several studies have tackled temperature effects on Li-ion intercalation into graphite but, until now, none has addressed a detailed atomistic study.

In this presentation, we introduce our most recent results regarding the kinetics of Li-ion (de)intercalation (from)into graphite from a theoretical-computational perspective, using the kinetic Monte Carlo (kMC) method. We have extended our previous work[1] to cover a complete set of properties at different temperatures, which can be contrasted with experimental results. In this respect, we have simulated cyclic voltammograms and potentiostatic steps, and calculated diffusion coefficients and exchange current densities for different states of charge at different temperatures. Some of these results are shown below.

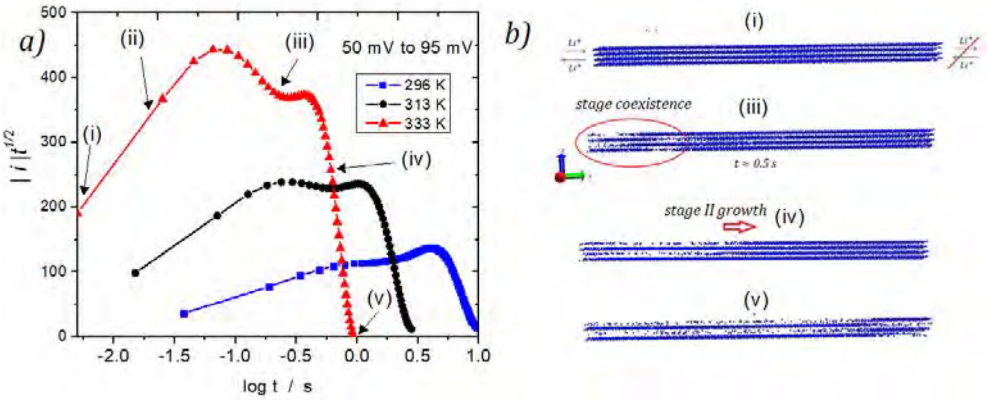

Figure: a) kMC chronoamperometric simulation results for a potentiostatic step from a potential where stage I is stable (50 mV), up to a potential where stage II is formed (95 mV) for three different temperatures. The principal events are indicated in the Figure form (i) to (v) for T=333 K. b) Snapshots showing some of the features labeled in Figure a.

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Towards Increasing the Operating Potential Window of Aqueous Supercapacitors through the Passivation of Carbon-based Electrodes by Electrodeposition of Poly(phenylene oxide)

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The main drawback of supercapacitors is their low energy density, which is mostly limited by the breakdown voltage of the electrolyte. Commercial devices typically use organic solvents, which can withstand up to 2.7 V, but are toxic and expensive[1]. Aqueous electrolytes would be a cheaper and environmentally friendly alternative if their electrochemically stable potential window ($\Delta V \approx 1V$) could be extended.

A conceivable way to achieve this is by electrodepositing an insulating material on the surface of the carbon-based electrode. Poly(phenylene oxide) was identified as a suitable candidate[2]. For a successful passivation, the deposited material must be thick enough to prevent electron transfer between the electrode and the electrolyte (>2 nm)[3] whilst simultaneously thin enough (<30 nm) to preserve the electrode's high surface area, indispensable for a high capacitance.

Preliminary results suggest a trade-off between capacitance and degree of passivation: a decrease in both oxidation and reduction leakage currents (measured at constant potentials and respectively associated to the oxygen and hydrogen evolution reactions) comes at the expense of a capacitance loss. This work will present results comparing differing polymer electrodeposition conditions and how these correlate both to the passivation of the electrode and to its performance metrics.

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Polymeric matrices as cathodes for Sodium-ion batteries - Electrochemical and pseudocationic doping behaviour characterization

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Sodium-ion batteries appear as an alternative more abundant, in terms of resource, and less expensive than the conventional Lithium-ion batteries, being used for applications where the weight and the specific energy are less determinant [1]. Their delay in commercialization is related to the delayed development of cathodes with capacities and performance similar to those achieved by commonly used materials in Lithium-ion batteries, since they must be designed for a larger size ion exchange [2]. The cathodic structure must be sufficiently flexible and stable, and extremely light [3] to compensate the total mass of the storage unit. An electronically conducting polymer with pseudocationic doping may fulfil this requirement. Here cations are exchanged during the polymer redox conversion.

Poly(3,4-ethylenedioxythiophene) doped with poly(styrene-4-sulfonate) (PEDOT:PSS) is a stable material that exhibits, in some extent, pseudocationic doping character, making it an attractive choice for cathodes in Sodium-ion batteries. Other doping polyanions such as Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) and Sodium dodecyl sulphate (SDS), may also impart, theoretically, a pseudocationic behaviour to the polymeric matrix.

Electrochemical techniques can provide information about the thermodynamics and kinetics of electroactive systems, but they do not resolve the structural and chemical modifications imparted by the mass transfer processes. So, the coupling of electrochemical methods with techniques sensitive to the structural and chemical changes caused by charge transfer phenomena on the electrode surface, will grant more information about the nature of the mass flow.

In this work PEDOT:PSS, PEDOT:PAMPSA, PEDOT:SDS, films were potentiostatically, galvanostatically and potentiodynamically synthesized onto platinum electrodes from aqueous solutions containing the monomer and the polyanion. The electroactivity and redox reversibility of these films was characterized by cyclic voltammetry in acetonitrile medium containing $NaClO_4$. Wettability was monitored by contact angle goniometry. The mass transfer phenomena taking place during the redox conversion of PEDOT:PSS films deposited with different thicknesses and at different temperatures, were investigated by coupling electrochemical methods with microgravimetry (EQCM) and Probe Beam Deflection (PBD). These techniques are well suited for measuring the mass flow, since they transduce both the ionic flow (probed by EQCM and PBD), and solvent molecules associated to the mechanical changes that occur during the redox conversion on the polymeric matrices (only probed by EQCM). By cooperatively using PBD and EQCM data, the ionic and the solvent mass flows were separately distinguished.

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Towards Active and stable $NiCo_2O_4$ catalysts for O_2 evolution and reduction

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It is particularly challenging to find a bifunctional catalyst capable of accelerating both O_2 evolution and reduction in aqueous solutions. The discovery of such a material would bring reversible fuel cells and metal air batteries much closer to technological fruition. Researchers have shown that both doped carbon and oxides show appreciable activity in short term tests, lasting hours. However, in a real device, such a catalyst will need to retain its activity over several years. Even the best bifunctional catalysts reported, thus far, would need to withstand an enormous potential window of at least 1 V. Nonetheless, to the best of our knowledge, little is known about the factors controlling the stability of bifunctional catalysts.

In the current contribution, we investigate $NiCo_2O_4$ and Co_3O_4 under both oxygen evolution and reduction conditions in 0.1 M KOH. When these materials undergo accelerated degradation test in a rotating disk electrode (RDE) configuration, rapid deactivation of the oxygen reduction is observed, as shown in figure 1. At the same time, this is accompanied by a significant increase in oxygen evolution activity and a shift in pre-catalytic redox peak. Herein, we employ a range of post-mortem techniques including inductively coupled plasma mass spectrometry (ICP-MS), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS), to understand the causes of the deactivation of $NiCo_2O_4$. Additionally, oxygen-electrode prototypes were manufactured and characterized in a half-cell configuration.

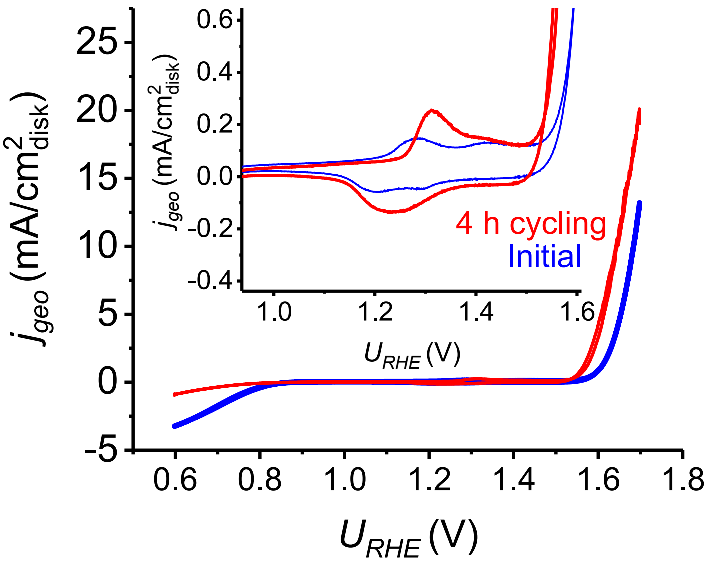

Figure 1 Cyclic voltammogram of $NiCo_2O_4$ in O_2 saturated 0.1 M KOH recorded at 10 mV/s, 1600 RPM and 25 $\mu g_{catalyst}/cm^2$. Blue line corresponds to the third scan and green line corresponds to the scan after cycling for 4 hours between 0.6 V_{RHE} and 1.7 V_{RHE} under the aforementioned conditions. Figure inset corresponds to a magnification of the cyclic voltammogram.

Acknowledgements: This work is supported by the project ''FLOWCAMP'' under the European union's innovation training network (grant agreement 765289)

Unidirectional Photosynthetic Complex Functionalization for Tunnel Current Distance Decay Spectroscopy

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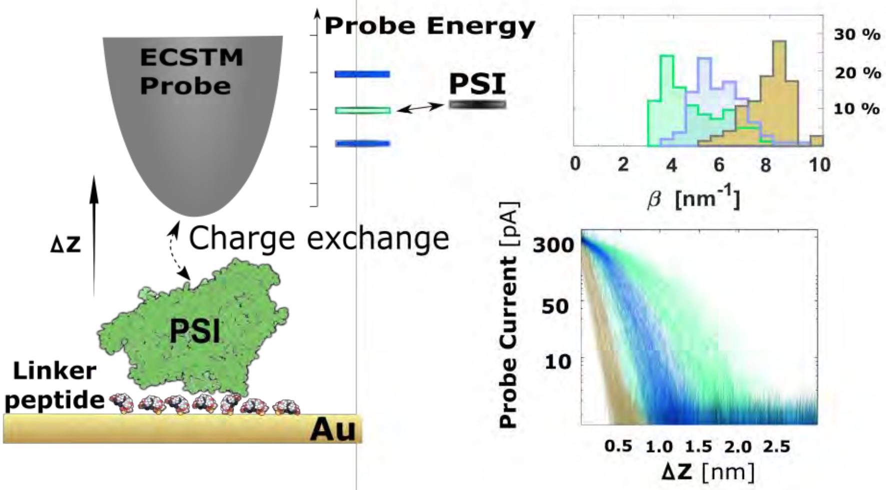
Interprotein electron transport (ET) is a key process for living organisms, playing a fundamental role in respiration and photosynthesis. ET processes between photosynthetic complexes and electron carrier partner proteins have been widely studied with bulk spectroscopic techniques[1], however the characterization of ET at the level of single molecules is limited. This is due in part to the lack of a well-defined experimental setup for protein orientation and current measurement. In this work, a peptide[2] that binds selectively to plant Photosynthetic Complex I (PSI) in is used to functionalize atomically flat gold monocrystal electrodes and to evaluate photocurrents by bulk photo-electrochemical experiments and ET by scanning probe techniques, atomic force microscopy (AFM) and electrochemical scanning tunneling microscopy (ECSTM). ECSTM-based spectroscopic measurements allow investigating the current decay distance[3] (β [nm^{-1}]) of PSI functionalized electrodes under electrochemical control. Mapping β over sample and probe potentials reveals enhanced charge exchange distance as probe potential is aligned with PSI's electron acceptor cofactor redox potential.



Left: Cartoon representation of peptide-PSI molecules absorbed on Au substrates in ECSTM experiment. Energy diagram displaying probe fermi level (green bar aligned, blue bars misaligned) and PSI ET cofactor redox potential (black bar). *Right bottom:* Semilogarithmic plot of tunnel current vs probe distance for aligned (green), misaligned (blue) probe potentials in peptide-PSI functionalized electrodes and bare Au control (yellow). *Right Top:* Histogram displaying current decay distance (β [nm^{-1}]) distribution for curves shown bellow.

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Tetraglyme - $Ca(TFSI)_2$, a non-monotonic liquid electrolyte

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Ca-ion batteries are considered among the most suitable candidate for post-lithium batteries as they present similar charge density and a large theoretical energy density 2.06 Ah/cm^3 [1]. Calcium, considering its reactivity and metal properties, is a safer element than lithium as it is less prone to burst in flame in contact with air and Ca platting-stripping reported so far did not show any dendrites growth demonstrating the safety of such technology to a moderate cost on electrolyte resistance [2]. In addition, Ca is the 5th most available element and evenly distributed on Earth compared to Li, 25th, making it a very promising alternative to Li [3].

Polymer electrolytes as compared to liquid electrolytes are easier to handle and shape on an industrial scale and tackle dendrite growth issues. Here we propose to pave the way to safe and efficient Ca-Polymer batteries avoiding the usage of organic based electrolyte. We investigated the most commonly reported polymer in the literature, PEO. A tetraglyme electrolyte coupled to a calcium salt ($Ca(TFSI)_2$) is used as preliminary study. This approach helps us to investigate the interaction between PEO polymer with calcium salt by means of ionic conductivity measurement carried out by Electrochemical Impedance Spectroscopy (EIS) and complementary techniques based on Raman and FT-IR spectroscopies. As can be seen in Figure 1, the conductivity response with respect to temperature is non-monotonic as normally expected from the Vögel-Tammann–Fulcher model. Several parameters could influence this behaviour among them, the viscosity of the electrolyte, the salt dissociation process, the crystallinity of the polymer etc. Such behaviour deserves a proper investigation to elucidate the process behind. We employed here *operando* Raman spectroscopy technique at specific temperatures to get insights into molecular structure of the species in solution (aggregates, solvated-Ca...). This method allows us quantifying the amount of Ca-diffusing species in the electrolyte and to correct Vögel-Tammann–Fulcher model, proposing then a new model better featuring the obtained conductivity measurements.

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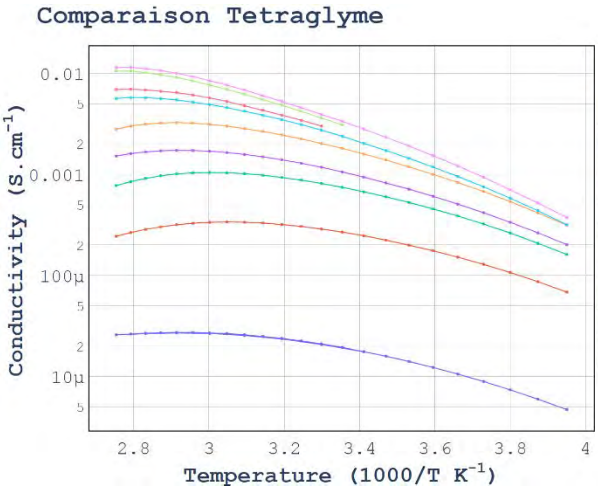

Figure ~~1~~1: EIS measured conductivity of $Ca(TFSI)_2$ tetraglym

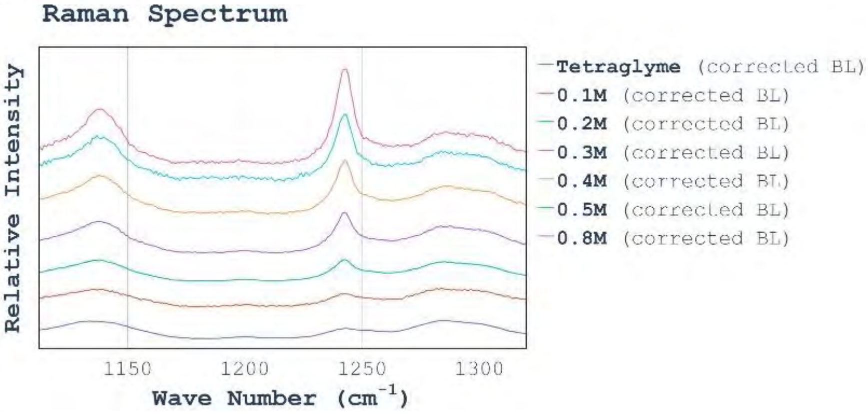

Figure ~~2~~2: Raman spectra of $Ca(TFSI)_2$ tetraglyme electrolytes

Soft X-Ray Microscopy of Manganese Hexacyanoferrate Cathode Materials for Lithium and Sodium Batteries

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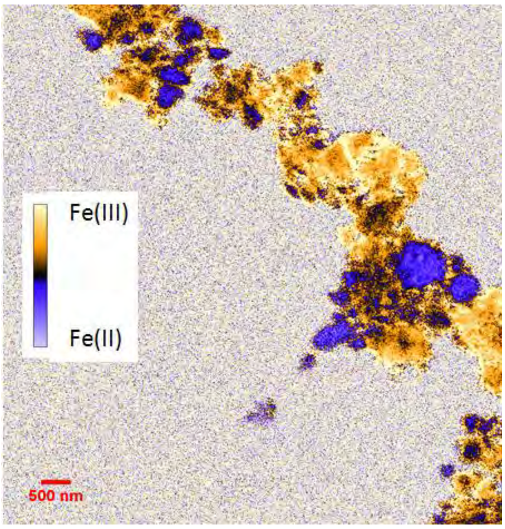
A very interesting, durable and cheap class of active intercalation cathode materials is represented by open-framework structures such as Prussian blue analogues (PBAs). Manganese hexacyanoferrate (MnHCF) with nominal formula $Na_2Mn[Fe(CN)_6]\bullet zH_2O$, only includes abundant elements and is safely and easily synthesized. The material features high specific capacities at high potentials when compared to other PBAs [1]. A combined XAS and XRD study has demonstrated that both Fe and Mn sites are involved in the electrochemical process but a capacity fading is observed during the charge and discharge steps, due to a Jahn-Teller (J-T) effect [2].

Using energy-dependent soft x-ray microscopy [3,4] in this study we reveal and visualize the spatial distribution of the oxidation state of Mn, Fe and N at different electrode composition and after 50 cycles in a Li and in a Na battery. The high-resolution access to the metal L edge provided complementary details on the metal-ligand characteristic to the one already available by hard x-ray absorption, while the images demonstrate particles at different state of charge, likely caused by J-T-related passivations, in particular in the cycled lithiated samples. This confirms the superior stability to sodiation and provides an important support for strategies aimed to the suppression of fading.



An example of data extracted from energy-dependent images at the Fe-L edge of a fully charged MnHCF electrode material in a Li battery after 50 charge-discharge cycles: maps of ratio between main spectral components highlighting distribution of different prevalent Fe oxidation states.

Acknowledgements

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Highly Corrosion Resistant Nb Coatings on Copper Bipolar Plates for Proton Exchange Membrane Electrolyzers

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Proton exchange membrane (PEM) electrolysis of water is a green procedure for hydrogen production, but to become competitive the cost of stack components, in particular bipolar plates (BPP) need to be reduced. This can be achieved by using coated low-cost materials as alternative to titanium. In this work, we report on the development of a highly corrosion-resistant coating deposited by vacuum plasma spraying (VPS) of niobium powder on copper substrate. Copper substrate has been used as a cost-effective replacement of titanium, commonly used to manufacture BPPs. The influence of the Nb coating thickness, given by the number of deposited layers (32, 16 and respectively 8 layers of Nb coating), on the corrosion resistance properties is investigated by electrochemical methods. Corrosion parameters of Nb coated samples have been determined from the Tafel plots shown in Fig. 1 and compared to those of pure metallic Nb, both before and after an accelerated stress test (AST) consisting in polarization at 2 V for 6 hours. Appropriate conditions for the corrosion and stress tests have been chosen to simulate the anode side environment of PEM electrolyzer under operating conditions and the degradation of the proton exchange membrane by fluoride release.

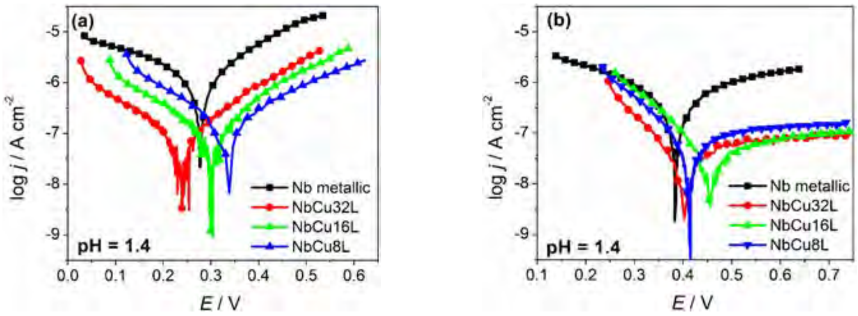

Figure 1. Potentiodynamic polarization curves (v = 1 mV s^{-1}) of metallic Nb and VPS Nb-coatings on copper in 0.05 M H_2SO_4 + 0.1 ppm F^- (pH = 1.4) (a) before and (b) after polarization at 2 V for 6 h, measured in O_2 saturated solution at 90°C.

Electrochemical impedance spectroscopy (EIS) is used to estimate the polarization resistance and thickness of Nb coatings. Interfacial contact resistance at different compaction forces is evaluated both before and after the AST. Post-test analytic is carried out by X-ray photoemission spectroscopy (XPS) and atomic force microscopy (AFM) measurements.

The results showed that even with a reduction of coating thickness from 130 to 30 µm, the highly corrosion resistance properties of Nb coatings are preserved, as proven by corrosion currents bellow 0.1 µA cm^{-2}. The AST at 2 V induces the formation of a passive oxide layer. Both EIS and XPS analysis gave a similar estimate of the protective oxide layer thickness of about 10 nm. The chemical composition determined by XPS shows the predominance of Nb_2O_5 in the outermost layer. These results demonstrate the possibility to reduce production cost of BPPs in PEM water electrolyzers by using alternative low-cost materials such as copper and substituting precious metals coatings with highly corrosion resistant coatings based on niobium.

Acknowledgment

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An Electrochemical Alternative to Reduce the Environmental Impact of Evaporitic Lithium Extraction from Brines. Stage I: Removal of Calcium and Magnesium

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In a context in which it is urgent to change the energy matrix dependent on fossil fuels for a more sustainable one, the reference to energy accumulation, electromobility and lithium is undeniable. Continental brines as present in a small region in South America (the Lithium Triangle), are the most abundant and the easiest to exploit with an evaporitic method [1]. Current practice is highly water and chemical intensive, and delivers besides lithium only waste to be landfilled [2,3]. Concerns about processing practices are growing, particularly with the local native population. As an alternative to the current extraction process, it is proposed an integrated membrane electrolysis process with three stages, each based on a water electrolyser with a side crystallizer. Lithium is present in diluted concentrations together with different ions, and it is imperative to fully remove both magnesium and calcium before lithium carbonate can be precipitated. In the stage I of this approach, hydroxyl groups are generated in situ in a two chamber electrochemical cell with a side crystallizer, omitting the need for chemical addition and not leading to substantial loss of lithium rich brine. The native brine is introduced into the cathodic compartment of a 2-chamber electrolyzer (AEM) like the one show in the figure. As the pH increases, $Mg(OH)_2$ and $Ca(OH)_2$ will quantitatively precipitate. The objective is to obtain these two salts with commercial value, avoiding that they remain as waste in the salar and minimize the amount of brine adsorbed on solids. Batch electrolysis experiments were performed and showed that for a native south american brine containing 3090 mg L^{-1} of Mg^{2+} and 685 mg L^{-1} of Ca^{2+}, 62 kWh m^{-3} are needed for the full removal of both cations when a current density of 223 A m^{-2}. It is necessary to remark that the Li^+ concentration in the brine is not affected. The first stage of this alternative process to the evaporitic method, not only performs the necessary removal of the divalent cations from the brine, but also allows obtaining magnesium and calcium compounds simultaneously, minimizing the production of waste.

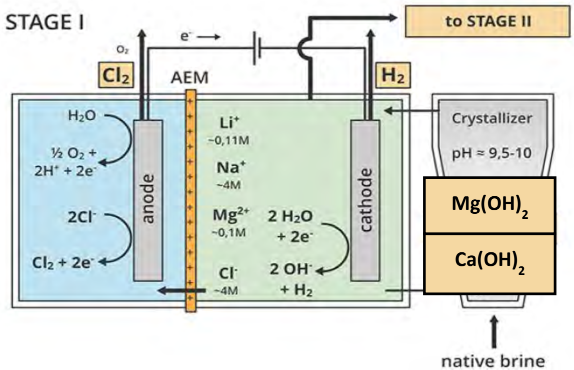

Figure: Scheme of the electrochemical cell of Stage I

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The Importance of the Electrolyte in Energy-Related Electrocatalytic Reactions: the Case of Bicarbonate

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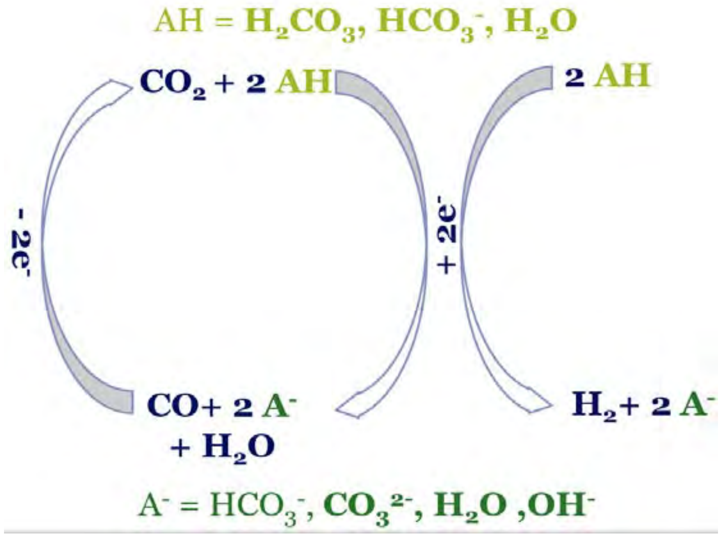
The nature of the electrolyte (pH, identity of buffer and its concentration) has proven to crucially affect electrocatalytic behaviour in a way that goes beyond simple water related equilibria. Herein, we expand the understanding of the effect of the widely employed bicarbonate electrolytes on hydrogen evolution reaction (HER), CO_2 electrochemical reduction (CO2RR) to CO and, viceversa, CO electroxidation to CO_2 (COOR).

We performed voltammetry measurements under well-defined mass transport conditions using a gold rotating disk electrode and rotating-ring disk electrode assembly changing the concentration of the bicarbonate electrolyte. Importantly, this systematic investigation reveals that carbonic acid and bicarbonate are viable proton donors for HER and CO2RR and that carbonate is an oxygen donor for COOR.

Additionally, probing the catalytic surface by in situ IR spectroscopy, we gain insights into the mechanism regulating the participation of bicarbonate-related species in the mechanism of HER, CO2RR and COOR.



Preparation of Co Single-Atom Nanozyme Based on Graphyne and Its Efficient Detection of H_2O_2

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Single-Atom Nanozyme (SAN) inherits the advantages of heterogeneous catalysts and homogeneous catalysts, not only has excellent activity and selectivity, but also achieves the maximum utilization efficiency of atoms [1]. Meanwhile, nanozymes with oxidoreductase-like activity, such as peroxidase, oxidase and catalase, have been extensively applied in biosensors, immunoassay, and therapy. Graphyne as a novel and unique two-dimensional planar carbon nanomaterial has excellent properties such as high electrical conductivity, high specific surface area, and stable structure, and can be used as an ideal biosensing platform [2]. Reactive oxygen species (ROS) such as superoxide ($O_2^{\cdot-}$) hydroxyl radical ($\cdot$OH) as well as H_2O_2 are present in numerous biological processes. However, the excessive generation of ROS would cause tissue injury and associated inflammation. Therefore, it is necessary to develop an ultra-sensitive and selective method to detect H_2O_2 in living cells.

In this work, graphyne was prepared by the mechanical milling method. First, the mixture composed of benzene and CaC_2 was put it into the ball milling chamber and ball milled for a certain period of time under certain ball milling conditions. Then, the product was calcined at 260°C and N_2 for 2 hours, and further washed by acid and dried to obtain graphyne. Next, Co-MOF@graphyne precursor solution was prepared by mixing $Zn(NO_3)_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, 2-methylimidazole and methanol. The mixture solution mildly stirred at room temperature for 24 hours, then the solution was transferred into a Teflon-lined stainless-steel autoclave, sealed, and heated to 120 ℃ for 6 h. The Co-MOF@graphyne was obtained by centrifugation, washed and dried in a vacuum oven at 60 ℃ overnight eventually. Scanning electron microscopy, transmission electron microscopy, and X-ray diffraction can be used to prove that the folded sheets of the catalyst are stacked. At last, Co SAN was successfully synthesized by high-temperature pyrolysis of Co-MOF@graphyne. After calcined at 900°C for 2h, Co single-atom nanozyme was obtained. At the same time, electrochemical tests also showed that the catalyst has oxygen reduction catalytic activity. For further research, the catalyst was tested for peroxidase-like enzymes to optimize pH, temperature, and incubation time for TMB substrate catalysis conditions.

The microbial corrosion of metals induced by sulfate reducing bacteria

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Microbiologically influenced corrosion (MIC) is one of the main reasons for the failure of engineering materials immersed in seawater. Sulfate-reducing bacteria (SRB) could induce corrosion on almost all metals, causing severe corrosion in almost all metals immersing in sea water. The corrosion of metal is closely related to the metabolic activity of SRB [1].

T. Gu [2] divided SRB induced metal corrosion into two forms: metabolite MIC (M-MIC) and extracellular electron transfer MIC (EET-MIC). M-MIC refers to the process in which the organic acids and other metabolites produced by SRB attack metals indirectly and accelerate corrosion by chemical reaction. Whereas EET-MIC refers to the process of direct corrosion of the metal by the SRB with the ability of extracellular electron transfer to obtain electrons directly from the metal surface and accelerate the corrosion of the metal. It is proved that the biocorrosion mechanism of metal is related to metal composition, environmental and bacteria. The corrosion mechanism of the same SRB strain is different for different metals. The corrosion of carbon steel caused by *Desulfovibrio vulgaris* strain SRB is mainly EET-MIC [3], while for copper alloy, the corrosion of *Desulfovibrio vulgaris* on copper alloy is mainly M-MIC [4].

To verify the MIC difference of 5052 and Al-Zn-In-Cd aluminum alloys by SRB strain *Desulfovibrio caledoniensis*, and the interaction between the aluminum alloys and *D. caledoniensis* metabolic activity. SRB growth curve and sulfate variation with and without aluminum were performed to find the effect of two aluminum alloys on SRB metabolic activity. Corrosion of 5052 aluminum alloy and Al-Zn-In-Cd aluminum alloy with and without SRB were performed. The results showed that both the presence of 5052 and Al-Zn-In-Cd aluminum alloy promoted SRB metabolic activity, with more significant effect was found on the 5052 aluminum alloy. The electrochemical results suggested that the corrosion of the Al-Zn-In-Cd aluminum alloy was accelerated substantially by SRB. EET-MIC is the most possible corrosion mechanism of Al-Zn-In-Cd aluminum alloy in SRB was EET-MIC, while M-MIC for 5052 aluminum alloy.

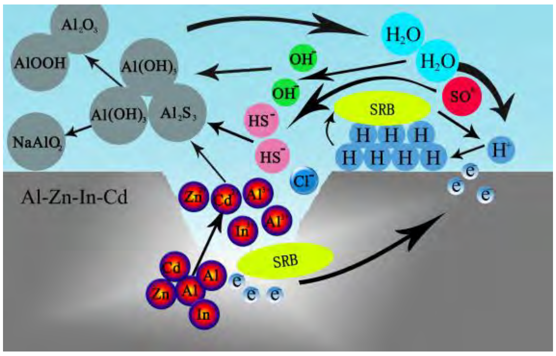

Fig.1 Schematic of the corrosion mechanism for the Al-Zn-In-Cd aluminum in SRB medium.

Acknowledgement

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Investigation of graphene and 1-ethyl-3-methylimidazolium tetrafluoroborate interfacial structure and capacitance temperature dependence

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Supercapacitors are electrochemical energy storage devices, where energy is accumulated at the double layer. To achieve better energy and power density, the electrolyte used in supercapacitors should have high electrochemical stability and ion conductivity. Room-temperature ionic liquids (RTIL) are novel compounds, which are considered as possible electrolytes due to their stability and low vapor pressure. As RTILs consist only of ions, the electrode-RTIL interfacial structure differs noticeably from other electrode-electrolyte interfaces. To study RTILs structure, molecular dynamics (MD) simulations are indispensable, as they allow modeling and investigating the interface on the atomic-scale without any undesirable impurities, which could alter the RTIL structure.

In this study, MD simulations have been used to evaluate the capacitance of an interface between model graphene electrode and 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid and to investigate its structural response to changes in temperature and potential. The aim of this study is to relate trends in interfacial capacitance dependencies to changes in ionic liquid's interfacial structure. This work shows that near the potential of zero charge, the increase in temperature decreases the capacitance due to increased thermal motion, which hinders the ordered packing of ions. Furthermore, characteristic saddle points in the capacitance-potential curve were related to the restructuring of the ionic liquid.

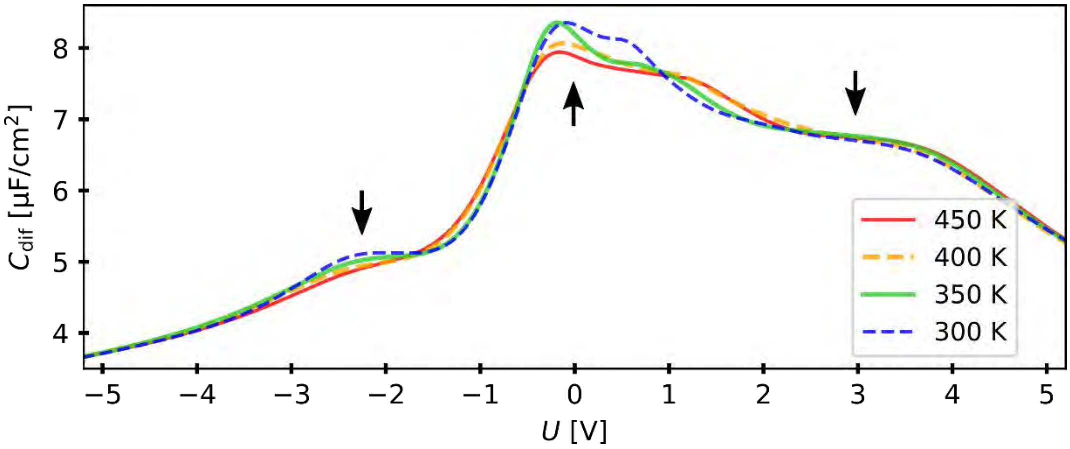

Figure 1. Capacitance-potential dependencies of studied temperatures in the range from −5 to 5 V. The potential axis (U) is shifted by the potential of zero charge of each temperature.

Acknowledgements: This research was supported by the Estonian Research Council (grants IUT20-13, PSG249, and PUT1107), the EU through the European Regional Development Fund (TK141 "Advanced materials and high-technology devices for energy recuperation systems"), and the Estonian–French cooperation program Parrot, funded by the Estonian Research Council and Campus France.

Photodegradation of 4-chlorophenol using composites g-C_3N_4/ZnO/carbon xerogel and ZnO/carbon xerogel as catalyst

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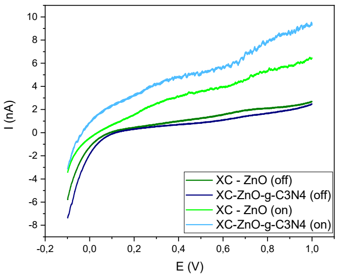
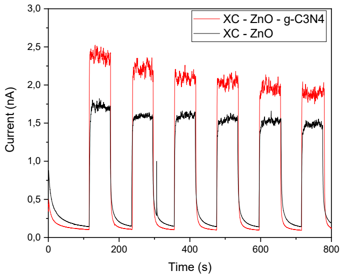
In the photocatalytic process for persistent organic pollutant degradation, the main aim is the increasing of the quantum efficiency diminishing charge recombination. The present study evaluates the effect of hybrids g-C_3N_4/ZnO/carbon xerogel and ZnO/carbon xerogel on heterogeneous photocatalysis in the degradation of 4-Chlorophenol. For the synthesis, 4.5 g of $ZnCl_2$ and 0.0689 g of g-C_3N_4 were solubilized in ethyl alcohol. Then, 1.5 ml of formaldehyde and 1.5 g of tannin were added and mixed with another solution with 4 g of KOH and the same solvent. The product was washed, dried in an oven (24 hours at 100 ºC), ground and sieved (325 mesh). The materials were calcined at 300 ºC for 30 min, under N_2 atmosphere. The XC/ZnO synthesis followed the same procedure. However, the g-C_3N_4 mass was not added. Electrochemical experiments were performed with linear linear voltammetry from -0.1 to 1.0 V on porous microlayers prepared with each material, deposited on a rotating ring electrode glass carbon. The electrochemical measurements were obtained with electrolyte K_2SO_4 0.05 mol L^{-1} (pH 2) using a potentiostat PGSTAT-bi-204N (Autolab/Metrohm) and RRDE (Pine Research).





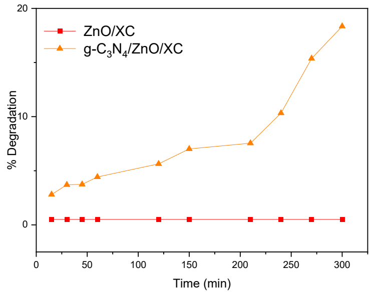


Figure 1: Linear voltammetry comparing under visible light and dark (on/off)
Figure 2: Photocurrent generation under pulsed irradiation for the materials prepared.
Figure 3: Degradation under visible radiation

According to Figure 1, the g-C_3N_4/ZnO/XC material shows higher current under visible light, implying in better charge separation and higher photocatalytic activity. Lower recombination rates result in higher photocurrent generations, and the g-C_3N_4/ZnO/XC shows superior photocurrent generation and high sensibility to light irradiation (Figure 2), which agrees with the photocatalytic efficiency shown in Figure 3, that exhibits 17% of photodegradation of 4-Chlorophenol. Therefore, this test proves the improvement of the efficiency of the catalyst under visible radiation with the presence of carbon xerogel and g-C_3N_4.

Acknowledgments

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A Metallic Copper Based Catalyst For The CO_2 Reduction To Formic And Acetic Acid

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Starting from the industrial revolution, the majority of the human activities have been tied to the use of fossil fuels. Electricity and heat production, intensive agriculture, industries and transportation are the main causes for the increase of gaseous CO_2 in the environment. With the so-called Paris Agreement, world leaders officially recognized the strong impact of anthropological activities on climate change and since then a great effort has been demanded to all fields of human sciences in order to guarantee a sustainable future for our society. In this framework, the concept of "artificial photosynthesis"[1] has gained momentum in view of a smart use of the atmospheric CO_2.

Inspired by the natural photosynthesis, carbon dioxide is converted back to chemicals and fuels by exploiting an electrochemical process[2]. This contribution describes the preparation of an easily synthesized catalyst made of metallic copper for the heterogeneous CO_2 reduction reaction (CO_2RR) in liquid phase in order to produce formic and acetic acid. The metallic copper-based catalyst was electrochemically synthesised on a gas diffusion layer (GDL) support made of carbon fibers as shown in Figure 1. Electrosynthesis allows the one step formation and deposition of the Cu film directly on the carbon paper substrate. Adapting an already reported procedure[3], the carbon paper electrode was pre-treated in 1M H_2SO_4 followed by soaking in pure EtOH. The role of the pre-treatment time on the surface properties of the support was thoroughly evaluated. In particular, the ratio between crystalline and amorphous carbon phases was optimised after investigation by Raman analysis on the single carbon fibers. Afterwards, electrodeposition of the Cu film on the carbon fibers support was achieved starting from an aqueous solution containing $Cu(NO_3)_2$ at room temperature and atmospheric pressure. The optimized catalyst was employed to carry out the CO_2RR in a typical H-Cell, in which a Nafion membrane divided the cathode side, containing the working electrode, from the anode side where a platinum gauze and Ag/AgCl electrode were used as counter and reference electrodes, respectively. The reaction was performed for one hour in $NaHCO_3$ aqueous solution. All the liquid products were collected in the catholyte and analysed by quantitative H^1-NMR, while the gas products were first collected in a gas sampling flask and analysed by Gas Chromatography. As first preliminary tests, several reactions were carried out both in continuous and discontinuous CO_2 flux at -1.1 V and -0.7 V vs RHE in which a CO faradaic efficiency (FE) up to 4,36% was obtained with a FE for H_2 evolution of 63,80% for the gaseous product. As for the liquid products, formic acid (up to FE = 4.46%) and acetic acid (up to FE = 6.69%) were obtained.

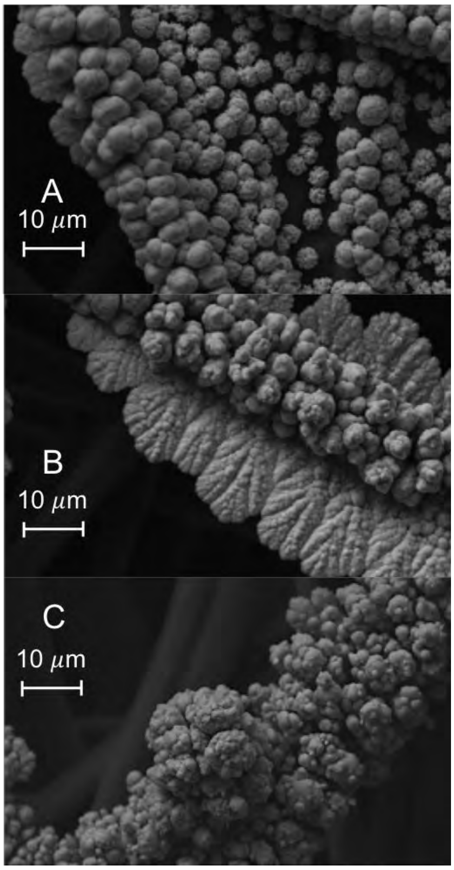

Figure 1 - Morphology of the metallic copper film on carbon GDL support (upper zone (A); middle zone (B) and lower zone (C)

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Electrochemical instabilities in lithium-oxygen batteries: The role of the redox mediator

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The increasing use of mobile devices and electric vehicles has brought as one of the greatest challenges of contemporary civilization the need for batteries that supplies this energy demand. Recently, spontaneous potential oscillations have been identified during the process of discharging lithium-oxygen batteries. Nonlinear dynamics in these systems are known to occur under conditions far from thermodynamic equilibrium as a result of the interaction between kinetic instabilities and mass transport properties. Understanding, therefore, the reaction mechanism can provide important clues to the birth and evolution of this temporal complexity, thereby enabling precise control and prevention of battery efficiency collapse. It was used lithium halides salts acting as redox mediator in the electrolyte composition, since during the oxidation of Li, the X^- of LiX is oxidized to X_3^- providing a decreasing in the charge overpotential. Besides that, the halides presence can act as a diffusional component that could help the emergence of electrochemical instabilities. Thus, it was assembled Li-O_2 batteries cells with and without LiBr which was submitted to different galvanostatic charge/discharge conditions in to comprise the effect of this species in the electrolyte. It was observed that the presence of bromide reduced the charge overpotential and improved the cyclability. Besides that, the role of applied current was evaluated and higher it was, less completed cycles were obtained. After determining an interval of current operation, galvanodynamic experiments will be conducted to obtain conditions under which spontaneous potential oscillations emerges. Thereby, it will be designed appropriated cells in which in operando experiments will be conducted to monitor spontaneous emergence of patterns with temporal resolution. Then, it is hoped to understand how experimental parameter can impact the nonlinear dynamics observed during the battery operation. Figure 1 presents the results obtained in cyclability Li-O_2 batteries tests with and without LiBr as redox mediator and using different galvanostatic conditions.

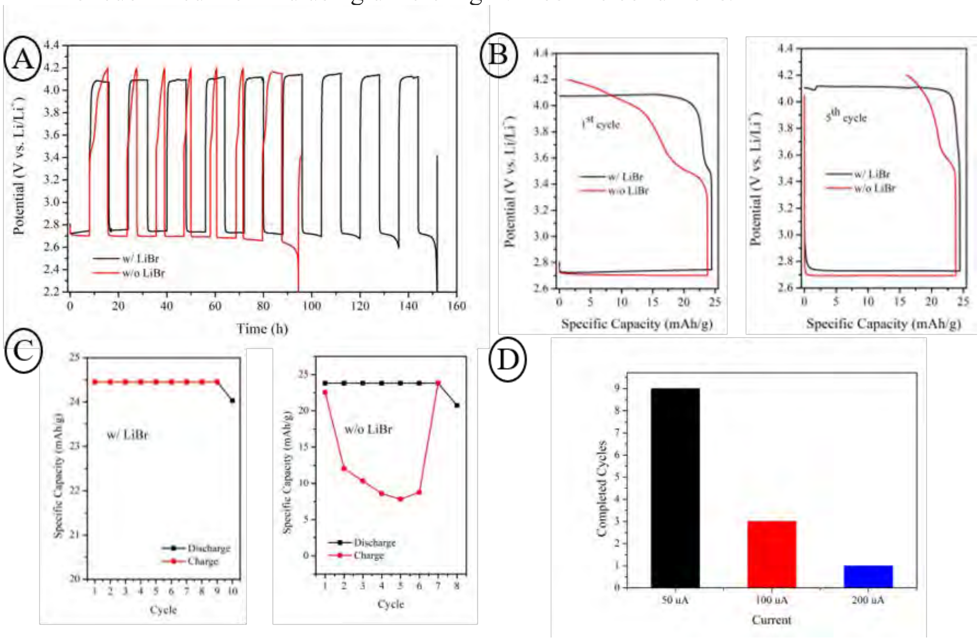

Figure 1: (a) Cyclability Li-O_2 batteries tests with different electrolytes: with and without LiBr in its composition. (b) 1st and 5th cycles for cyclability Li-O_2 batteries tests with different electrolytes: with and without LiBr in its composition. (c) Evolution of Li-O_2 battery capacity with and without LiBr in the electrolyte composition. (d) Cyclability Li-O_2 batteries tests in different galvanostatic conditions with LiBr in the electolyte.

Use of $FeMnO_3$ as a Catalyst in the Water Splitting Reaction

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Conversions between O_2 and H_2O are an important part of many renewable energy production technologies. Alkaline water splitting electrolysis (Oxygen Evolution Reaction-OER) is considered as an effective and environmentaly acceptable route for the production of hydrogen and oxygen gas required as resources for energy production via fuel cells. Also, with the approaching commercialization of PEM fuel cell technology, search for active, inexpensive non-precious metal ORR catalyst materials to replace currently used Pt-based catalysts is necessary in order to reduce the system cost.

These renewable energy solutions require active, stable and low-cost electrocatalysts. In this work, we present our results on iron manganite synthesized by a relatively new synthesis method as a catalyst material for both OER and ORR reactions.

$FeMnO_3$ was synthesized via a sol-gel combustion synthesis process using glycine as fuel and nitrate ions as oxidizing agents and iron nitrate nonahydrate and manganese nitrate hydrate as precursors. After vivacious combustion a black ash-like powder was obtained. The amorphous powder was then sintered at 800 °C for 6 hours and structurally, morphologically and texturally characterized [1]. XRD showed phase content of a pure bixbyite cubic structure. The structure recorded with TEM and FESEM can be described as a plate-like, net-like formation, with particles ranging from 0.2 to 1 μm. About 10-20% of the particles' surface area was interconnected, as estimated from TEM images. With Kubelka-Munk function extracted from the light absorption spectrum the band gap of the synthesized powder was determined to be 1.69 eV, slightly lower than reported in literature.

$FeMnO_3$ was tested as a catalyst anode for both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) via linear voltammetry (LV) with Nafion as the carrier polymer agent, carbon black and graphene oxide. In OER $FeMnO_3$ with nafion as a carrier polymer agent exhibited 4.4 A g^{-1} mass activity and 3.3 A cm^{-2} surface activity, while in ORR activity was 2.4 A g^{-1} and 1.2 A cm^{-2}. Charge transfer resistance was measured by electric impedance spectroscopy (EIS) and mathematically fitted and was found to be relatively low (OER: $R_{CT}=27\ \Omega$ at E=1.15 V, ORR: $R_{CT}=230\ \Omega$ at E=-0.5 V). Electrode stability was tested with chronoamperometry (CA) measurements during 1 hour and the material maintained 57% of the initial current jump at the end of the trial period at the potential of E=1.15 V.

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Atom-scale dispersed palladium in a conductive $Pd_{0.1}TaS_2$ lattice with a unique electronic structure for efficient hydrogen evolution

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ABSTRACT: Noble metal catalysts have extraordinary catalytic activity but suffer from high cost; therefore single atom catalysis attracts tremendous attention. Here, we propose atom-scale dispersed palladium (Pd) in a layered TaS_2 lattice to form new compounds of Pd_xTaS_2, whose crystal structure was resolved by powder X-ray diffraction. The electrical conductivity of metallic $Pd_{0.1}TaS_2$ (1.36×10^4 S m^{-1}) is twice as large as that of TaS_2 (6.18×10^3 S m^{-1}). This compound applied as a new electrocatalyst for the hydrogen evolution reaction (HER) exhibits excellent catalytic performance with an onset overpotential of 77 mV, superior to those of other catalysts such as TaS_2 (295 mV) and Pd-loaded TaS_2 (114 mV). Density functional theory calculations reveal that the interaction of Pd-4*d* and Ta-5*d* orbitals results in the upshift of the Fermi level (TaS_2 *versus* $Pd_{0.1}TaS_2$) to decrease the barrier height for the HER. Furthermore, the hybridization of Pd-4*d* and S-3*p* orbitals builds up pathways along the c axis to improve the conductivity and promote HER performance. It is noted that the amount of Pd used in $Pd_{0.1}TaS_2$ is only 4 *wt.*%, compared with 20 *wt.*% in commercial Pd/C catalysts, which is beneficial for its practical application.

Carbon Nanomaterial-modified Inkjet Printed Silver Nanoparticle Paper Electrodes for Adsorptive Stripping Voltammetry of Ni(II)-chelate complexes

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The development of low-cost, disposable electrode materials has been at the forefront of sensor technology in recent decades. Paper, offers possibilities for multi-functional, disposable and economically friendly sensing capabilities and has proved to be a suitable reagent storage and substrate material in paper-based analytical devices (PADs). In this work, we report a simple inkjet printing procedure on photographic paper for the fabrication of single analyte electrochemical sensors. A three-electrode systems, consisting of a 3 mm diameter working electrode (WE), a counter electrode (CE) and a reference electrode (RE) were prepared by inkjet printing of silver conductive inks. In a second step, modification of the working electrode surface with (a) an electrochemically reduced graphene oxide, gold nanoparticle (ERGO-AuNP) film, to improve electrode sensitivity and (b) a nafion dimethylglyoxime carbon black (N-DMG-CB) ink, as an environmentally friendly, metal-free approach was employed. Electrical and topographical characterization of the printed layers was performed in the fabrication process. Printing of Ag-NP ink showed good resistivity (1.8 – 6.3 Ω) on photographic paper. The prepared printed paper-based electrodes (PPE) offer a quantitative analysis of Ni(II), based on the accumulation of $Ni(dmgH)_2$ complexes at the modified electrode surfaces by square-wave adsorptive cathodic stripping voltammetry (SW-AdCSV). Instrumental parameters including deposition potential and deposition time were optimized for both electrochemical sensors. Improved sensitivities were achieved at the modified integrated electrodes with limits of detection (LOD) of 32.19 and 48.01 $\mu g\ L^{-1}$ for the ERGO-AuNP-CC-Ag-PPE and N-CB-DMG-Ag-PPE respectively. This is well below the EPA and WHO standards of 0.1 $mg\ L^{-1}$ or 0.1 ppm for Ni^{2+} in drinking water.

Exploring the Interfacial Behavior of Aluminum Electrodes in Ionic Liquids: an Impedance Study

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The expansion of renewable energy production and the growing number of energy storage devices demand improved and low-cost electrochemical energy storage technologies. To meet the future needs of energy storage, novel materials with high energy densities, readily available raw materials and safety are required [1]. Aluminum as the most abundant metal in the earth's crust attracts the electrochemists' attention, especially as the established recycling technology and price make aluminum very cost efficient. However, for aluminum as an anode in secondary battery some challenges remain. Pristine aluminum is intrinsically protected by a passive Al_2O_3 layer. This layer has two effects: making redox potential more positive and limiting the exposure of the active surface [2]. Furthermore, when aluminum has been used as the current collector in supercapacitor, the contact resistance increases over time.

Room temperature ionic liquid (IL) electrolytes present new possibilities for nonaqueous aluminum ion battery owing to their tunable physicochemical properties. One of main advantages is the high electrochemical stability [3]. However, several disadvantages of using ILs as electrolytes for aluminum batteries remain. One is the decomposition and dissolution of the cathode materials in chloroaluminate-based ILs. Another is the possibility of side reactions in chloroaluminate-based ILs. Worse, the chloroaluminate-based ILs are highly corrosive, hygroscopic and viscous, all of which aggravate their limitation as an efficient battery electrolyte [2]. Therefore, it is of importance to explore suitable non chloroaluminate-based ILs toward to aluminum battery electrodes.

Considered the above statements, it is of importance to address the covering layer when establishing an electrochemically active interface between the Al anode and the IL electrolytes. After all, electrochemical reactions at the interface reflect the fundamental understanding of the interfacial processes governed by double layer formation at electrode|IL interfaces. To overcome those obstacles, the interfacial behavior of Al and Al(111) electrodes in ILs is studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods. Three different IL anions have been chosen for this study with the same cation 1-ethyl-3-methylimidazolium (EMIm), namely, bis(trifluoromethylsulfonyl)imide (TFSI), tetrafluoroborate (BF_4) and perchlorate (ClO_4). From the EIS results, relatively low capacitance values for capacitance vs. potential curves in the three studied ILs have been observed. The average capacitance value in this study are much lower than what have been shown in literature [4]. This implies that the fully metallic Al surface cannot be obtained from the ILs under this study. Interestingly, within the negative polarization range, the average capacitance values in three ILs can be clearly distinguished from the different anions. That is, it shows the lowest average capacitance values for the large TFSI anions. It suggests that, with regard to the ILs themselves, the interaction of IL and aluminum surface can form an anomalous layer structure which limits the exposure of the single crystal Al electrode. The stability of this surface layer has been explored.

Acknowledgements

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New sodium orthoferrite synthesis route for green sodium-ion batteries

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The growing demand for lithium-ion batteries may, in the future, limit the available lithium resources, significantly influencing the cost and the own survival of technology. Therefore, new materials are investigated to replace the non-abundant and expensive raw materials that constitute the available cathode active material on lithium-ion batteries.[1] Among the emerging technologies, the one that uses sodium ion and iron stands out. Sodium orthoferrite, $NaFeO_2$, shows polymorphism with the α-phase stable up to 770 ºC and the β-phase stable at higher temperatures. The phase α-$NaFeO_2$ presents a lamellar structure that allows the diffusion of sodium ions in two dimensions, enabling its use as a cathode of Na^+ based batteries.[2] The investigation of this material is essential for the commercial application of these batteries. Thus, the aimed of this study was to synthesize α-$NaFeO_2$ via sol-gel route, not yet described in the literature, and to verify its crystallographic, morphological and electrochemical properties. The effect of the concentration of chelating agent (citric acid), of the calcination temperature and time, on the synthesis, were studied. X-ray diffraction shows the tendency to the formation of the α-phase in the ratio of 1:2 of citric acid and metals. By Rietveld's refinement of the calcined sample at 600 ºC for 4 days it was verified that the only phase containing the iron was α-$NaFeO_2$ with contamination with Na_2CO_3 of less than 5%. Spherical grains of the order of 200 nm were observed by scanning electron microscopy. Using the BET method, it was observed that the α-NaFeO2 phase synthesized by the sol-gel route had a surface area 4 times greater than that described in the literature for solid state synthesis. Electrochemical performance measurements revealed a charge capacity for the first cycle of about 113 $mA\ h\ g^{-1}$ in the potential range of 1.00 to 4.00 V *vs.* Na^+/Na. Even higher discharge capacity values, as well as superior electrochemical performance can be achieved by improving the synthetic parameters of the new route are in progress.

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Molecular simulation of lithium metal deposition

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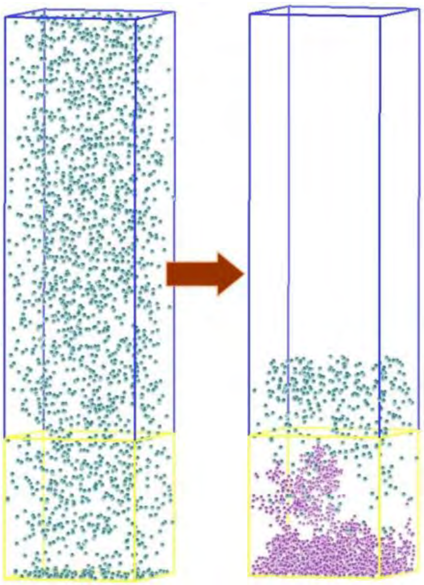

Lithium metal is considered the ultimate anode for energy-storage systems for its extremely high theoretical specific capacity (3860 mAh g−1), the lowest redox potential (−3.040 V vs the standard hydrogen electrode) and a low gravimetric density (0.534 g cm−3) [1]. However, the main issue associated with this electrode is the growth of metal dendrites, also known as high surface area lithium (HSAL), during charge/discharge cycles. Therefore, there is a great interest in the study of the mechanism of HSAL formation and the effect of the different variables involved. The final goal is the possibility to tune these variables to control the formation of HSAL. Such control remains elusive probably because it requires an important feedback between theory and experiments. Molecular simulations could help to improve this feedback, although the construction of an *ad hoc* model that connects the simulations parameters with the experimental measures is required. We have developed a computer model based on that of Mayers et. al. [2] to simulate the HSAL growth. One side of the simulation box, say the bottom, is considered an ideal electrode where lithium ions can be reduced and deposited. On the opposite side, the simulation box is connected to a constant density reservoir of lithium ions that maintain the system at a constant chemical potential. The motion of lithium ions is integrated using the Langevin equation that, together with the reservoir, set the system in the μVT thermodynamic ensemble. The deposition is a random event with probability P that may occur when a lithium ion approaches the implicit electrode or a previously deposited metal atom. This probability P can be connected to the experimental cell current. In this work we present the effects that different P values have in the resulting HSAL morphologies. The study of other processes like dissolution or surface diffusion within this model, and further extensions, are discussed.

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Electrochemical Flow Reactor for the Sustainable Extraction of LiCl from Natural Brines

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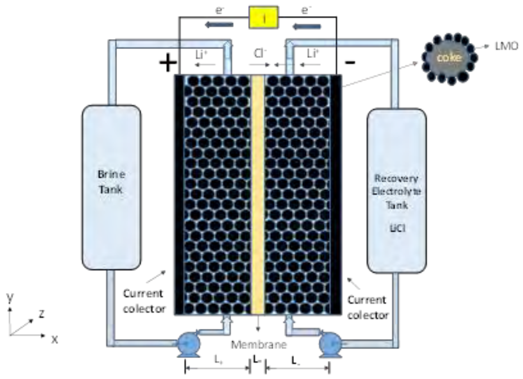
We consider an electrochemical flow reactor with two compartments separated by an anion (chloride) selective membrane. The electrochemical reactor is comprised of two 3D compact porous bed electrodes with conducting petroleoum coke particles covered by the spinel oxide $LiMn_2O_4$. The cathode is a lithium deficient $Li_{1-x}Mn_2O_4$, and the anode is $LiMn_2O_4$, which exchange lithium ions. The architecture of this flow electrochemical reactor is similar to a vanadium flow battery and operates by a rocking chair lithium intercalation mechanism of lithium ion batteries



The reactions in each electrode are the following:

In the negative electrode,

$$LiMn^{III}Mn^{IV}O_4 \rightarrow Li_{1-x}Mn^{III}_{1-x}Mn^{IV}_{1+x}O_4 + xLi^+ + xe$$

in the positive electrode:

$$LiMn^{III}_{1-x}Mn^{IV}_{1+x}O_4 + yLi^+ + ye \rightarrow Li_{1-x+y}Mn^{III}_{1-x+y}Mn^{IV}_{1+x-y}O_4 \; (0 \leq x \leq 1, \text{ and } y \leq x)$$

We will present digital simulation (COMSOL® 5.2a) results of the interfacial intercalation, ion diffusion in the $LiMn_2O_4$ particles, ion transport by diffusion and migration under tertiary current distribution and liquid electrolyte circulation under constant current applied to the reactor. We analyze the experimental and digital simulation results with plots of cell voltage vs. time (or charge) under constant current and lithium concentration with a potentiometric ion selective electrode.

From the simulation results we obtain plots of concentration distribution in the electrolyte and electric potential in the electrodes. We have also studied the effect of Li^+ concentration, flow velocity, current density, etc.

We will present results of LiCl extraction in two steps, from natural brines of Olaroz and Hombre Muerto (Argentina), Uyuni (Bolivia) and Atacama (Chile) which demonstrate the method works with different natural brine compositions.

Method for the Accurate Prediction of pK_a and Electron Transfer Potentials from ab-initio Calculations

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The ability to efficiently and accurately predict acid dissociation constants (pK_a) and electron transfer (ET) potentials is critical for the success of computational methods in electrochemistry. Proton coupled electron transfer reactions are typically modeled using the computational hydrogen electrode A comparable simple and efficient procedure is, however, still missing for pure electron transfer reactions. Here, typically the absolute potential is used to compute the redox potential. While this method is computationally efficient it interferes with the inherent cancellation of errors from density functional theory (DFT) and implicit solvation models. The alternative use of a well studied and computationally undemanding electrochemical reference reaction such as the oxidation of a simple organic molecule, which would allow for this cancellation of errors, is limited by the almost complete absence of reliable electrochemical measurements for suitable compounds. This is opposed to the dissociation constants of acids which can be obtained experimentally with high accuracy for almost any material.

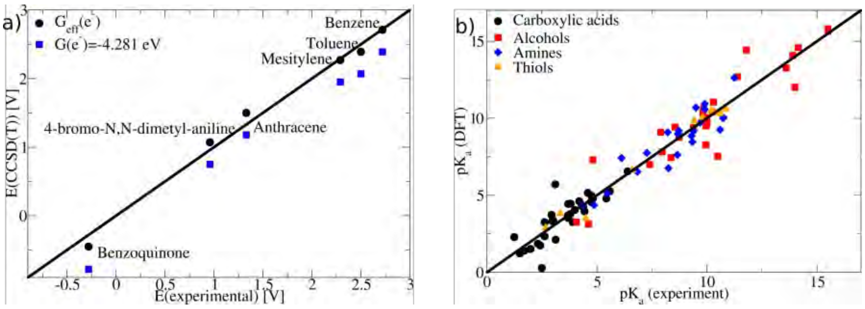

*Figure 1: : a) Comparison of ET potentials computed using coupled cluster CCSD(T)/Def2-TZVPP with experiment. b) Comparison between computed acid dissociation constants (PBE0/6-311++G**/SMD) using the effective proton solvation energy $G_{eff}(H^+)$ after correction for chemical similarity and experiment.*

In this contribution we will show a thermochemical cycle which connects the pK_a with electron transfer and proton coupled electron transfer reactions. This allows us to determine an effective absolute potential $G_{eff}(e^-)$ and an effective proton solvation energy $G_{eff}(H^+)$ for any ab-initio or DFT method using the experimentally well defined pK_a of an arbitrary acid as reference reaction. $G_{eff}(e^-)$ can be used to predict the ET potential. A comparison of high level coupled cluster CCSD(T) calculations with experimentally well characterized ET reactions on small organic molecules shows that our method is, due to the superior cancellation of errors, able to predict energetics of ET reactions with high accuracy (Figure 1a). In a subsequent benchmark with respect to CCSD(T) results the best performing DFT functionals were extracted.

In addition to computing ET potentials our method also allows for the prediction of pK_a values using the effective proton solvation energy $G_{eff}(H^+)$. The accuracy of the method can be increased further by including corrections for the differences in chemical similarity between the functional group considered in the reference reaction and those of the molecule of interest. The accuracy of the effective proton solvation method was tested for a set of 73 organic molecules with varying complexity. Our computations indicate that pK_a values can be predicted with chemical accuracy (Figure 1b).

Synthesis of activated carbon using sugarcane bagasse

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In the process of electrochemical synthesis of hydrogen peroxide, the main area is the development of the electrodic material modifier for oxygen reaction reduction (ORR) with the formation of H_2O_2. The present study evaluates the viability of using activated carbon from sugarcane bagasse (SCB) as organic carbon source, for the H_2O_2 electrochemical generation.
The sugarcane bagasse was crushed, washed and impregnated with H_3PO_4 solution (0%, 5%, 10%, 20%, 30%, 40% and 50%) for 3 days. Then, these materials were dried in an oven (3 hours at 150 °C) and calcined at 700 °C for 1 hour (heating rate 5 ºC min^{-1}). At the end of the process, the calcined material was ground to obtain a fine powder. For electrochemical tests, porous microlayers were prepared with each material following the literature[1]. Electrochemical experiments were performed with linear sweep voltammetry on microlayers of different materials deposited on an electrode rotating ring (Pt)-disk(GC). The electrochemical measurements were obtained with electrolyte K_2SO_4 0.05 mol L^{-1} (pH 2) using a potentiostat PGSTAT-bi-204N (Autolab/Metrohm) and RRDE (Pine Research).

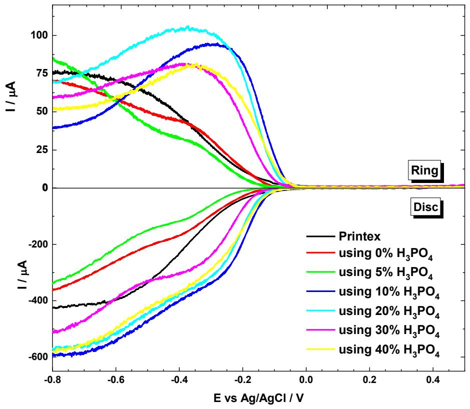

Figure 1: LSV catalyst (ORR) of SCB impregnated with H_3PO_4 and calcined at 700 °C for 1 h under uncontrolled atmosphere

The initiation reaction occurs from the potential of -0.15 V and the current diffusion limit starts from -0.3 V and -0.4 V for material with 10% and 20% of H_3PO_4, respectively. The analysis of the graph was based on the values above -0.2V, because it is possible to notice that with smaller values, the potential tends to zero volts, forming less hydrogen peroxide. By comparing the carbon values of SCB with acid to that without acid and Printex, it is already possible to see from the current values the effectiveness of the application of the acid. Note two important information in Figure 1, first is the maximum current reached in the ring, which the material with 20% acid reached approximately 110 μA compared to the Printex with 75 μA. Another important point is the potential at which these currents were observed, the SCB with 20% H_3PO_4 reached the maximum current at -0.4 V while the Printex reached the maximum current at -1.0 V.

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Acknowledgments

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Lignin-derived carbons for supercapacitors and microbial fuel cells

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Porous carbons are key electrode components of many electrochemical energy storage/conversion systems. With the aim of exploiting wasted derived by biomass plants, here, lignin was valorized as raw material for the production of carbons with tailored porous texture for a use in electrical double layer capacitors (EDLCs) and microbial fuel cells (MFCs). The lignin-derived activated carbon (LAC) was generated by a one-step carbonization route using $KHCO_3$ as mild activating agent. Different lignin-to-$KHCO_3$ ratios were explored. The performance of the LAC carbon electrode was investigated in supercapacitors and for oxygen reduction reaction (ORR) at neutral pH. LACs obtained at biomass/$KHCO_3$ mass ratios of 1:0.5 and 1:2 (LAC-0.5 and LAC-2) comprised of mesopores and micropores and displayed BETs of 1558 m^2g^{-1} and 1879 m^2g^{-1}, respectively. LAC-2 exhibited a superior specific capacitance and ORR electrocatalytic activity. A symmetric supercapacitor with LAC-2 electrodes and 2.5 M KNO_3 electrolyte displayed a specific capacitance of 28.5 F g^{-1}, corresponding to an electrode specific capacitance of 114 F g^{-1}, a specific energy of 10 Wh kg^{-1} and a specific power of 397 W kg^{-1}. A capacitance retention of 84.5% after 15,000 charge-discharge cycles was demonstrated. The ORR kinetics at LAC samples were studied using a rotating disk electrode (RDE) in a neutral medium. LAC-2 showed the highest electrocatalytic activity. The better performance of LAC-2 vs LAC-1 can be explained with a better interconnected porous network and higher surface area that make that the former lignin-derived porous carbons suitable electrode materials for dual applications, EDLCs and MFCs..

Acknowledgments

This research was carried out under the Italy-South Africa joint Research Programme (ISARP) 2018-2020 (Italian Ministers of Foreign Affairs and of the Environment). The South African Research Chairs Initiative of the Department of Science and Technology and the National Research Foundation of South Africa (Grant No. 61056) is also acknowledged.

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Electrodeposition and Electrochemical Characterisation of Thin Nickel Overlayers on Au(111)

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Nickel is widely used in energy storage and conversion, e.g. nickel-iron, nickel-cadmium, and nickel-metal hydride batteries. The behavior of nickel electrodes has been investigated extensively. However, a detailed understanding of surface processes on the atomic level is still missing.[1,2] In particular, there have been only a few fundamental studies of nickel single crystal electrodes related to their electrochemical oxidation.[3] The initial stages of the electrochemical deposition of nickel have been studied on Au(111).[4] The electrochemical fabrication of thin nickel overlayers on Au(111) and their electrochemical characterization have been investigated in detail.

The nickel overlayers have been electrochemically deposited onto Au(111) from a 0.01 M $NiSO_4$ solution and subsequently characterized by cyclic voltammetry in a 0.1 M KOH solution. Metallic nickel is highly sensitive to oxidation by ambient air, which requires very careful handling of the electrodes.[2,3] The transfer of the electrode from one electrochemical cell to the other has been done under inert gas atmosphere to guarantee stability and electrochemical performance of the nickel electrode surfaces. Figure 1 shows the current density-potential curve of a nickel overlayer on an Au(111) single crystal in comparison with the behavior of Au(111) and Ni(111) in 0.1 M KOH. The study of nickel monolayers on Au(111) helps to identify surface and bulk contributions of Ni electrooxidation. In addition, relations between structure of the Ni electrodeposit and its electrochemical behavior are addressed.

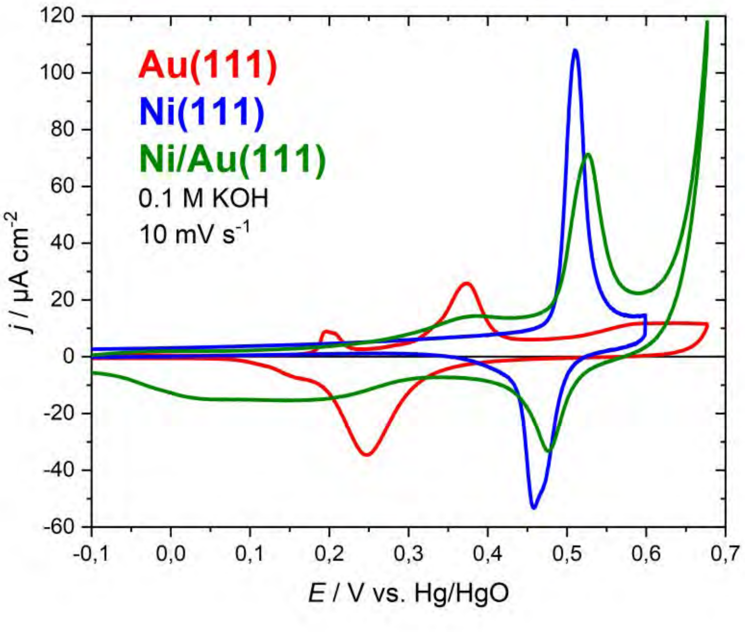

Figure 1: Cyclic voltammogram of a nickel overlayer electrodeposited onto an Au(111) single crystal in 0.1 M KOH in comparison with Ni(111) and Au(111). Scanrate: 10 mV s^{-1}.

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Electrospun nickel manganite ($NiMn_2O_4$) nanofibers for temperature and humidity sensing applications

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Monitoring temperature and humidity/moisture is widely present in many domestic, industrial and medical applications. Nickel manganite, a transition metal oxide cubic spinel oxide, has been previously applied as a Negative Temperature Coefficient (NTC) ceramic material for temperature sensing due to its stable characteristics, low room temperature resistivity and moderate temperature sensitivity. Electrospinning is a method used to obtain nanofibers from a solution using electric force generated by high voltage. Nickel manganite ($NiMn_2O_4$) nanofibers were obtained by electrospinning and subsequent calcination at 400 °C. TG/DTA of the as-spun fibers was performed. X-ray diffraction analysis confirmed the formation of a cubic spinel structure. The fiber surface area and pore size distribution was estimated using nitrogen porosimetry. The morphology of as-spun and calcined nanocrystalline nickel manganite nanofibers was analyzed by Scanning Electron Microscopy (SEM). Initial investigation of the material constant (B) of the nickel manganite nanofibers applied as paste on test interdigitated electrodes on alumina substrate, dried at 100 °C was determined as 4379 K in the temperature range 20-50 °C and temperature sensitivity of -4.95%/K at room temperature (25 °C) and is comparable with commercial devices using spinel based NTC ceramics, confirming the potential for application in flexible temperature sensors. Complex impedance monitored at room temperature (25 °C) in a climatic chamber in the relative humidity range 40-90% decreased noticeably with increase in humidity showing that this material can also be applied as a humidity sensor.

Electrochemistry and thermoelectrochemistry of ‘super-concentrated’ ferricyanide/ferrocyanide systems

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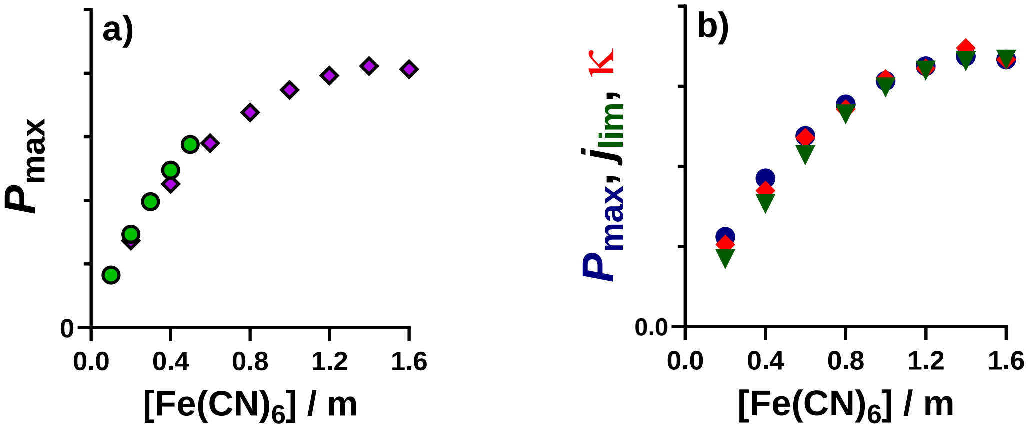
Internationally, most energy is produced from heat sources, such as fossil fuels or nuclear, where the vast majority of this is lost as low-grade waste heat. [1] However, waste thermal energy can be converted directly into electricity using electrochemistry. This can be achieved by an entropically driven thermoelectrochemical process, which uses a dissolved redox couple sandwiched between two electrodes held at different temperatures, as part of a thermoelectrochemical cell (or thermocell). [2] The $[Fe(CN)_6]^{3-/4-}$ redox couple is arguably the most investigated redox couple in thermocells; this is due to the high Seebeck coefficient, and fast-reversible electrode kinetics, resulting in high power outputs. [3] The power density of $[Fe(CN)_6]^{3-/4-}$ thermocells is known to scale proportionally with concentration [3], where the saturation limit at ambient temperature in aqueous solvent of the typically employed $K_{3/4}[Fe(CN)_6]$ redox couple is *ca.* 0.2 M of both $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$. A combination of alkali metal cations in the $[Fe(CN)_6]^{3-/4-}$ thermocell is known to have a synergistic effect on both the thermodynamics (Se coefficient) and kinetics (electrocatalysis) of the system.

Therefore, we investigate ‘super concentrated’ $[Fe(CN)_6]^{3-/4-}$ thermocells using a combination of the $K_3[Fe(CN)_6]$ and $Na_4[Fe(CN)_6]$.[4] Whereas K_3/K_4 have a combined solubility of 0.4 m (molal) when K_3/Na_4 are combined they have a combined solubility of 1.6 m, effectively 4-fold higher. Ultimately, the higher concentration increased the current and the power produced by the thermocell significantly, however, at very high concentrations, a plateau was also observed meaning that a 4-fold increase in concentration only resulted in an *ca.* 1.5x increase in the power produced. In order to investigate this phenomena, conductivity, viscosity, cyclic voltammetry simulation and rotating disk electrode (RDE) voltammetry were conducted and the results will be discussed in this poster.



a) Graph showing maximum power changes with concentration of $[Fe(CN)_6]^{3-/4-}$ (K_3/K_4 Green, K_3/Na_4 Purple) **b)** Graph showing power (blue), limiting current (green) and conductivity (red)

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Two-step modification of planar Au SPE's towards amperometric Lactate detection

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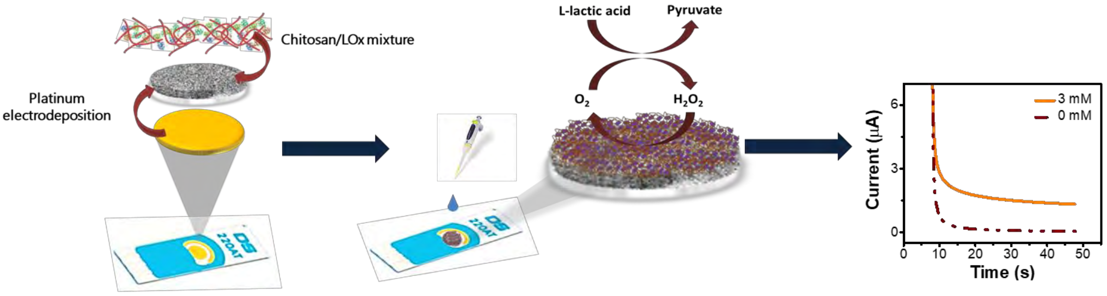

Graphical Abstract

Abstract:

Blood lactate levels are used as an indicator of physical fitness as well as being of interest in the clinical diagnosis of a number of conditions. An increase in lactate levels has been linked with hypoxia [1], endotoxic shock [2], sepsis [3], diabetes [4] in addition to cancer diagnosis [5]. Blood lactate levels of a healthy human at rest have been reported at 0.5 mM - 2 mM [4]. Here we report a two-step modification with Platinum and a Chitosan/Lactate oxidase mixture to the gold planar screen printed disc electrode (Au/Pt/CHT-LOx) for electrochemical enzymatic lactate detection. This Au/Pt/CHT-LOx electrode was examined using chronoamperometry at 0.3 V vs. Ag SPE. The modified electrode responds linearly from 0 to 3 mM of lactate. The relative standard deviation (RSD) towards detection of a 1mM lactate concentration was determined to be 6.52% (n=4) demonstrating a good level of reproducibility. The sensor was challenged against the following interfering species: 5 mM glucose, 0.05mM L-ascorbic acid, 0.2 mM Uric acid and 10 μM acetaminophen. A 2.5 mM lactate response increased by 2 % in the presence of interfering species (n=4). The operational stability was assessed by carrying out 10 successive measurements in 1 mM lactate on three electrode surfaces. The RSD of each respective electrode was calculated to be 8 %, 4.7 % and 5 % indicating excellent re-usability.

Key Words: Electrochemical, Enzymatic, Lactate, Lactate Oxidase

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Potentiometric investigation of steel-assisted synthesis for gold nanoparticles production

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Gold nanoparticles (AuNPs) are the most ancient metal nanophase ever used and they are among the most common metal nanomaterials employed even today [1]. Among the methods for metal nanoparticles preparation, the chemical reduction of metal ion species is widely applied, based on the use of precursor and reducing/stabilizing agents. Recently, few research groups have proposed steel corrosion to assist the synthesis of metal nanoparticles starting from a precursor salt, typically $HAuCl_4$ [2,3]. In this approach, stainless steel can be used as removable solid reductant in the aqueous preparation of gold nanocolloids. This innovative method is very easy, quick, cost-effective and scalable allowing the synthesis of highly stable nanoparticles without additional capping agents. However, the mechanisms behind this reaction are not yet fully understood. To date, two distinct reaction pathways have been proposed. According to the first hypothesis, Cl^- penetration through the passivating oxide layer on steel is invoked, thus assisting steel surface corrosion [2]. The second one considers that hydrogen, which is formed as a consequence of the reduction of protons mediated by the steel substrate, reduces $AuCl_4^-$ ions yielding AuNPs [3]. In order to support the system investigation, we carried out the syntheses recording the open circuit potential (OCP) to potentiometrically explore the electrochemical behavior of steel and track the solution potential [4]. The *operando* OCP monitoring has never been examined and it is useful to assess the role of steel corrosion in the synthesis mechanism. In particular, the experimental setup for AuNPs syntheses and simultaneous recording of OCP values consisted of a two-electrode cell, including the stainless steel working electrode mounted on a rotating bar and an Ag/AgCl (KCl sat.) reference electrode. The recorded potentials during OCP measurements are a combination of reduction potential of $AuCl_4^-$ ions in solution and corrosion potential of stainless steel. In addition, different experimental settings that may influence the synthesis process and final nanoparticle properties were evaluated. Particularly, the role of Cl^- concentration, pH of the precursor solution, as well as steel composition are described. In general, different initial potential values and OCP trends were found, depending on experimental settings. The OCP decrement towards more negative values reported in some cases suggested a higher trend to oxidation and a progressive dissolution process of steel metals such as iron, chromium and nickel. This phenomenon promotes the reduction of Au^{3+} to Au^0, thus leading to AuNPs synthesis. Hence, the different corrosion behaviors were examined and the best conditions for the AuNP synthesis were established. These findings were supported by a deep spectroscopic and morphological characterization carried out to correlate the synthesis parameters with the AuNPs characteristics. will be discussed. In this communication, results of OCP experiments together with the complete analytical characterization will be presented demonstrating the validity of this approach.

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Highly active Ag/C nanoparticles containing ultra-low quantities of sub-surface Pt for the electrooxidation of glycerol in alkaline media

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Abstract

In this work we synthesized carbon supported Ag 20% (w/w) nanoparticles (NPs), and then we successfully decorated them with ultra-small (0.8%) quantities of Pt. The resulting electrocatalyst was tested for the electrooxidation of glycerol. XRD, ICP, XPS, TEM and electrochemical characterization strongly support that the Pt atoms are located at the sub-surface of the Pt(0.8%)Ag/C and that the electrochemical excursion until the Ag_2O formation induces the Pt atoms segregation activating the material for the hydrogen evolution reaction, hydrogen Oxidation reaction and electrooxidation of glycerol (figure 1a). We showed that the Pt atoms of our catalyst are one order of magnitude more active (in terms of mass activity) than Pt/C commercial catalyst (Figure 1b).

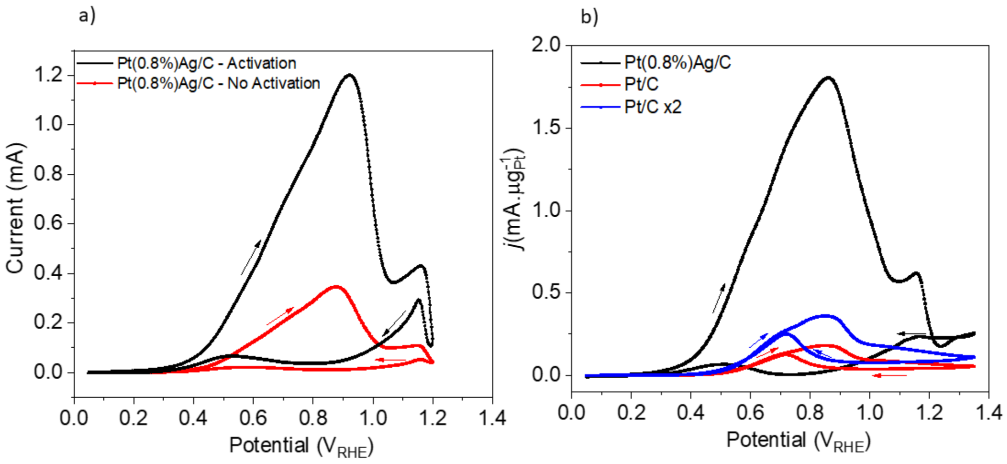

Figure 1. Cyclic voltammograms obtained in 0.5 mol.L^{-1} NaOH and 1.0 M GlOH solution at scan rate 10 mVs^{-1} for Pt(0.8%)Ag/C activation and no activation (**a**) and Pt(0.8%)Ag/C and Pt/C Normalizing the data by the Pt mass (**b**).

By performing *in situ* FTIR measurements, electrolysis experiments and HPLC analysis, we showed that both catalysts form mainly glycerate and lactate[1], but Pt/C is more prone to poisoning and to break the C-C bond of the molecule to form carbonate[2]. We suggest that this different behavior is attributed to the high dispersion of the Pt atoms on Ag NPs. The lower probability of finding neighboring Pt atoms (compared to Pt/C) diminishes the formation of multiple bonded intermediates, which are precursors for the formation of carbonate and some poisoning intermediates[2].

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Effect of Cerium Nitrate on Corrosion Inhibition of Mild Steel in Different Components of Brine Solution

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Enhanced oil recovery (EOR) technology is getting more attention, in which water flooding is one of the most common, economical, and efficient methods for secondary oil recovery. Generally, produced water or formation water from the oil well used for this purpose. This water consists of an aggressive ion such as chloride, sulfate, and bicarbonate ion that cause the failure of oil well pipelines. There are many techniques used to mitigate the corrosion inside the pipes. Meanwhile, cerium nitrate inhibitors are considered as an efficient inhibitor to use for different metals and alloy due to its low cost, abundance, and eco-friendly. Owing to this, cerium nitrate is investigated as an inhibitor for various solutions such as Sodium chloride, sodium sulfate, and sodium bicarbonate solution.

Further, immersion test, electrochemical polarization test, and electrochemical impedance spectroscopy are employed to study the corrosion inhibition. Consequently, the morphology and composition of inhibitor film formed on the metal surface are determined by SEM, XRD, and FTIR and discussed in detail. Based on all the results, cerium nitrate inhibitor found to be an efficient inhibitor in the case of bicarbonate and sulfate ion-containing solution with higher inhibition efficiency as compared to the chlorine ion-containing solution. The results proved that cerium nitrate inhibitor could be utilized as promising corrosion inhibitors for various industrial applications.

~~The Wet Etching Approach for Decreasing the Thickness of Mesoporous Silica Films Generated by Electrochemically Assisted Self-Assembly~~

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~~The design of new electrochemical sensors and their nanometrenanometre scale modification is always a challenge for scientific community. Electrode coatings based on organized mesoporous silica films (MSFs) is one of the branches which develops rapidly with respect to all demands[1]es[1,2]. Combining electrochemistry and sol-gel process (electrochemically assisted self-assembly, EASA[23]), the thin (thickness around 100 nm[34]) organized films with hexagonal mesostructure and pores, perpendicularly oriented to the electrode support cylindrical pores (2-3 nm in diameter), they can be obtained. The thickness of deposited film is important, since its decrease may help to facilitate mass transport through to non-inert silica poresTdecrease [56], to lower the unwanted accumulation of analysed probe and, hence, to gain in electrochemical response.~~

~~Under the operated conditions (100 mM TEOS, 32 mM of CTAB, 10 s of deposition at -1.3 V potential applied to ITO electrode), the generation of defectless and homogeneous MSFs gives a rise to a minimum thickness equal to 79±10 nm. With the aim of obtaining the thinner film, post-treatment by ammonium fluoride solution[7] (also known as wet etching procedure) was applied to deposits[4]. It was shown, that the evolution of the film thickness measured by profilometry ,with[8]time with etchant insideis the function of contact time between the etchant and silica sample. The presence of covalently bonded to MSF surface ferrocene species did not interfere the silica dissolution. Instead, the reduction of its electrochemical response while etching appeared to be another way to follow the film thickness decrease[5]. Transmittance electron microscopy characterization demonstrated that the vertically oriented hexagonal structure is still preserved after 1 hour reaction with 0.05M NH_4F while tAfter treatment, tt[9].he thickness becomes a third less relatively to the initial value.~~

~~The practical application of wet etching approach will be checked on sensor for glyphosate (GLYP) detection. The potential hazard of GLYP and the presence of the secondary amine in its structure makes it a perfect candidate to be analyzed by the electrochemiluminescence (ECL) reaction with tris(2,2'-bipyridine)ruthenium(II) ($Ru(bpy)_3$)[6], grafted on MSF surface. Typically, the best yields of the ECL reaction between GLYP and $Ru(bpy)_3$ are observed at pH 7-10[7], but deprotonation of pesticide in these conditions leads to negatively charged analyte, what complicates its mass transport through negatively charged silica film channels. Therefore, the effect of film thickness will be taken into the account and its decrease by wet etching is expected to improve the performance of ECL sensor.with~~

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~~8 N. Vilà, J. Ghanbaja, E. Aubert and A. Walcarius, *Angew. Chemie - Int. Ed.*, 2014, **53**, 2945–2950.~~
~~9 T. Sikolenko, C. Despas, N. Vilà and A. Walcarius, *Electrochem. commun.*, 2019, **100**, 11–15.~~

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Wet Etching Approach to Tune the Thickness of Electrochemically Assisted Self-Assembly Mesoporous Silica Films

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The design of new electrochemical sensors and the continuous improvement at the nanometre scale stays a challenge for scientific community. Electrode coatings based on organized mesoporous silica films (MSFs) is one of the approaches[1,2]. By combining electrochemistry and sol-gel process (electrochemically assisted self-assembly, EASA[3]), the obtained thin (thickness 80-100 nm[4]) organized films with hexagonal mesostructure and pores, perpendicularly oriented to the electrode support (cylindrical shape with 2-3 nm diameter), they represent an interesting new class of nanomaterials. The thickness of deposited film is an important parameter influencing the mass transport ~~to~~through the electrode surface specifically because silica is a reactive material (silanol groups). The thickness decrease of silica film should reduce the diffusion constraint through the film while keeping the advantage of the coating (molecular sieve[5], preconcentration[6]) and, hence, gain in electrochemical response.

The electrogeneration of defectless and uniform MSFs onto ITO electrode (100 mM TEOS, 32 mM of CTAB) requests a minimum deposition time equal to 10 s at -1.3 V. The resultant thickness is 79±10 nm. Post-treatment of the silica film is needed to decrease its thickness. The selected approach is the drop wet etching with ammonium fluoride solution[7]. Profilometry measurements and electrochemistry monitoring (with neutral or ionic probes, or ~~with~~onto ferrocene grafted MSF[8]) report the decrease of the thickness in function of contact time with etchant and its concentration. The influence of the presence of CTA^+ kept inside the silica pores is demonstrated and discussed. Transmittance electron microscopy proved that the well oriented pores and regular mesostructure of the film is still preserved after 1 hour reaction with 0.05M NH_4F. After treatment, the coating is three times thinner than originally[9].

Field Code Changed

In view of possible application, the detection of glyphosate by electrochemiluminescence (ECL) with functionalized mesoporous silica films is also evaluated. Tris(2,2'-bipyridine)ruthenium(II) complex is grafted onto silica pores by click reaction to limit the mass transport to the pesticide diffusion through the film. The resulting ECL signal is discussed in function of the MSF thickness.

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Synthesis of GONR/Pt nanocomposites for visible light-enhanced methanol oxidation reaction in an alkaline solution

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We have studied graphene oxide nanoribbons (GONRs) for a variety of applications since 2011. [1-14] In this study, Pt nanoparticles with the average diameter of around 4.3 nm were adsorbed on GONRs prepared with different microwave powers to form GONR/Pt nanocomposites. The GONR/Pt nanocomposites were then characterized by transmission electron microscopy, x-ray diffraction, Raman, x-ray photoelectron spectroscopy, and photoluminescence. For electrochemical measurements, the nanocomposites were drop casted on screen-printed carbon electrodes for methanol oxidation reaction (MOR) in an alkaline solution (1.0 M CH_3OH + 1.0 M KOH) with or without the illumination of a blue light. It was found that our Pt/GONR(200 W) exhibits the remarkable photo-enhanced MOR current density in cyclic voltammograms and the number is even higher than that of Pt/g-C_3N_4. [15] The photoeletrochemical activity of Pt/GONR nanocomposites could be due to the semiconducting nature of GONRs that may change along their processing parameters. More details of GONR/Pt electrocatalysts for photoeletrochemical MOR will be presented and discussed in this conference. These investigations on novel nanomaterials may benefit the further development of direct alkaline methanol fuel cells.

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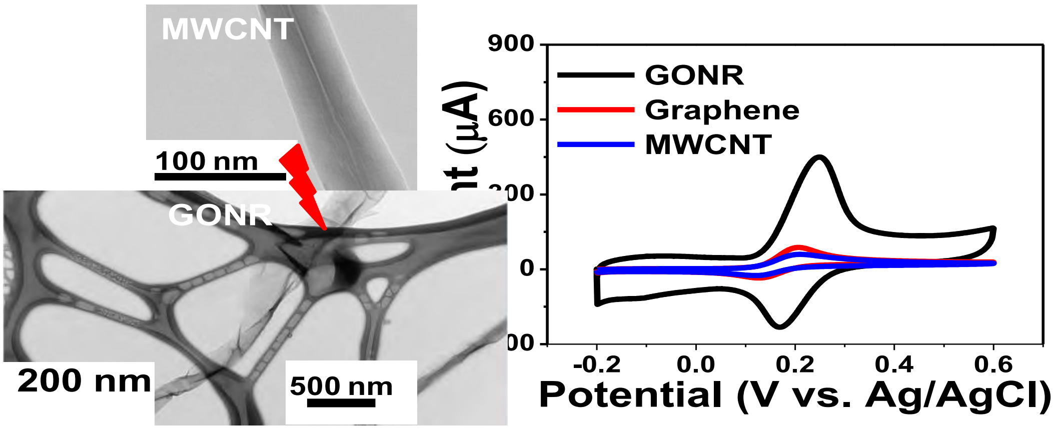

Fig. 1. Microwave-assisted synthesis of core-shell MWCNT/GONR heterostructure for electrochemical

detection of ascorbic acid, dopamine, and uric acid. [1]

Studies Concerning the Electrochemical Corrosion and Electrochemical Cutting of Iron Silicon Alloys

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Sheet metal cutting is widely used in the tailoring of metal parts. The mechanical cutting, techniques, milling sawing, guillotine, punching, etc., are widely used but they often lead to localized material structure modifications (accumulation of unwanted residual stress) within the cutting area. Nor new techniques (Water Jet Machining, Abrasive Jet Machining, or Laser Beam Machining) cannot eliminate the disadvantages of the mechanical cutting [1]. Electrochemical Cutting (EC) can remove the disadvantages of the mechanical methods and ensure a high precision. EC is based on the controlled anodic dissolution of metals (Cu, Ni, Fe, Ti etc.) and their alloys [2]. In this research, the electrochemical corrosion and cutting of iron silicon alloys (ISA) were investigated.

The demand of soft materials like ISA in various applications like electrotechnical industry/electric power distribution systems, has greatly increased. Such materials have augmented magnetic properties due to grain size, crystallography of the material, the level of impurities (silicon concentration - up to 6.5% Si) but they lack in electrical conductivity [3, 4, 5].

The purpose of this research is to investigate the corrosion behavior during the EC of ISA in different types of electrolytes like sodium nitrate, sodium sulfate and sulfuric acid (in small concentration), in mono-component solutions and in mixtures, in order to setup an efficient (short time and small current demand) EC cutting process.

Optimal potential range, current densities, and electrolyte composition for the EC process of three types of ISA were established based on cyclic voltammetry and polarization curves.

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Improvement of Analytical Characteristics of Lactate Biosensors Using Prussian Blue Nanoparticles and Siloxane-Perfluorosulfonated Ionomer Membranes

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Prussian Blue is recognized as the most advantageous low-potential transducer for hydrogen peroxide [1]. Due to high catalytic activity and selectivity which were comparative with enzyme biocatalysis, we even denoted Prussian Blue as ‘artificial peroxidase’. Recently we reported Prussian Blue based nanozymes [2] defeating natural peroxidase in term of their catalytic activity. Nanozymes were characterized by true enzymatic properties: (i) enzymatic specificity (an absence of oxidase-like activity) and (ii) an ability to operate in physiological solutions.

In contrast to bi-enzyme biosensors we propose the nanozyme-enzyme based ones substituting the enzyme peroxidase with the more active and stable Prussian Blue nanoparticles.

The procedure of sensor development involves the simple drop-casting of the nanozyme suspension onto the electrode surface with subsequent drying. The resulted modified electrodes characterized with even higher sensitivity to hydrogen peroxide as compared to conventional Prussian Blue sensors.

For immobilization of lactate oxidase the improved protocol with enzyme exposing to water-organic mixtures with the high content of organic solvent proposed earlier has been used [3]. Since lactate oxidase is among the less stable enzymes, further stabilization of the enzyme containing membranes is required for multiused commercial biosensors.

For this aim we've investigated the stabilization of the lactate oxidase containing siloxane membranes [4] with Nafion analogue – perfluorosulfonated ionomer (PFSI). The perfluorosulfonated ionomer induce the decrease of sensitivity of the resulting biosensors caused by negatively charged substituent able to shield the enzyme active site. However, it is possible to observe an absolute maximum of sensitivity. At the same point the apparent Michaelis constant of the corresponding biosensors displays the minimum for non-zero PFSI content in the membranes illustrating the highest affinity of the immobilized enzyme to lactate.

Operation stability of lactate biosensors has been evaluated as the number of lactate injections (0.2 mM) in flow-injection mode remaining the response at the level of 95% from its initial value. The highest operational stability has been registered for biosensors made from the mixture of 1.5 % γ-aminopropyltriethoxysilane and 0.2 % Nafion, which corresponds to the extremes in sensitivity and Michaelis constant. Operational stability of the corresponding biosensor in terms of the number of lactate injections remaining 95% activity (81 ± 4 injections) is almost 3 times higher as compared to the biosensor made without perfluorosulfonated ionomer (28 ± 3 injections). At the same time the decrease in sensitivity compared to the biosensors made without PFSI is only 35%.

Hence, an addition of 0.2% of PFSI to the membrane-forming mixture provides the significantly improved stability of the resulting siloxane based enzyme containing membranes. Thus improved protocol for lactate oxidase immobilization has been used for elaboration of the nanozyme-enzyme biosensor.

The resulting nanozyme-enzyme lactate biosensor displays twice higher sensitivity ($> 0.2\ A\cdot M^{-1}\cdot cm^{-2}$) compared to the Prussian Blue film based one [5]. Nanozymes “artificial peroxidase” are expected to find wide use in elaboration of oxidase based biosensors.

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Bi-metallic IrSn catalysts supported on Montmorillonite - efficiency towards OER in PEMEC

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Global environmental concerns and increasing energy demands are the main drive to move from fossil fuels to renewable energy (such as wind or solar). The world has strong need for reliable, cost-effective, and renewable clean energy sources. Hydrogen shows a great potential as a fuel for a sustainable energy future. The electrolysis of water is the most attractive technology to produce carbon-free energy when coupled with electricity produced from renewable sources. However, a major challenge remains the high overpotential at the oxygen electrode and the use of expensive noble metals (e.g., Ir or Pt).

In this work bimetallic nanosized IrSn powders were synthesized and studied as anode electrocatalysts using non-carbon catalytic support (one cheap natural phyllosilicate mineral montmorillonite (MMT)) and reducing the expensive noble metal Ir by cheaper one (Sn). IrSn/MMT catalysts with different Ir:Sn ratio were obtained by sol-gel technique. Thus, prepared catalysts were characterized in terms of structural (XRD) and morphological (TEM) features. Their electrochemical behavior and catalytic activity towards the oxygen evolution reaction were investigated by cyclic voltammetry, steady state polarization curves and electrochemical impedance spectroscopy in a laboratory polymer electrolyte membrane electrolysis cell (PEMEC) at elevated temperatures 20oC – 80oC using. The efficiency of most active catalyst IrSn/MMT was compared with that of a previously investigated Ir/MMT catalyst [1]. It was found that Bi-metallic IrSn catalyst supported on Montmorillonite has a larger developed surface area (fig.1) and higher catalytic activity concerning OER. Due to synergetic effects between iridium and the used interactive oxide support, the loading of the noble metal can be reduced essentially without sacrifice of efficiency thus, decreasing the cost of catalysis.

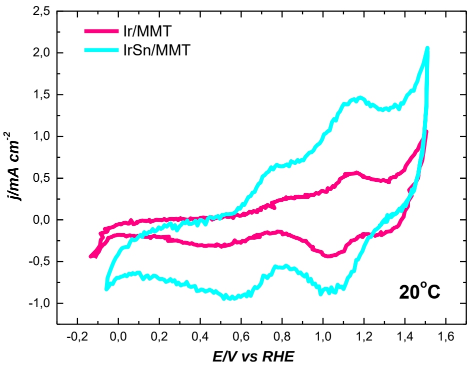

Figure 1: Cyclic voltammograms of the catalysts Ir/MMT and Ir18Sn12/MMT under study in PEMEC at 20^{o}C; potential scan rate 100 mV s^{-1}.

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Exploring High-activity Copper Doping Zirconia Catalysts for Methane Electrochemical Conversion at Room Temperature

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Recently, a lot of research has been done on the conversion of CH_4.[1] Compared to photo-catalysis and thermos-catalysis with precious metal catalysts and high reaction temperatures, the electro-catalysis path which are always performed at room temperature demonstrates more potential. In this regard, the electrochemical oxidation and conversion of CH_4 to commodity chemicals, such as wide-application liquid alcohols, shows obvious economic benefit and high energy/conversion-efficient. Zirconia (ZrO_2) has rich Lewis acid active sites and huge electron acceptability, showing a remarkable adsorption capacity of CO_3^{2-}.[2,3] Thereby, zirconia-based hybrids have attracted a lot of attention and have made some breakthroughs. Transition metal oxide doping ZrO_2 forming TMO/ZrO_2 compound demonstrates the potential of methane oxidation with CO_3^{2-} at room temperature. Compared to NiO and Co_3O_4, copper-based (Cu) catalysts have a high activity and a long-term durability on forming liquid and gas organics of C1 catalysis reaction system (CO_2 reduction reaction) at room temperature.[4] Hence, we present a facile strategy of using Cu ions doping ZrO_2 to activate the hybrid activity by manipulating its crystal and electronic structure. As except, the unique cylindrical ZrO_2:CuOx catalyst shows remarkable CH_4 oxidation performance with large current density differences (13.35 mA cm^{-2}) and long-term electrochemical stability (negligible attenuation (10 %) after 48 hours). According to theoretical and experimental observations of the CH_4 oxidation on ZrO_2: CuOx hybrid, the high activity and durability of the hybrid should be attributed to i) strong synergistic-coupling effect; 2) the unique doping structure forming favorable electronic and crystal structure; 3) fast oxidation reaction mechanism by shortening the reaction path. The mechanism could be described as that ZrO_2 facilitating CO_3^{2-} adsorption, then CO_3^{2-} as the oxidizing agent source rapidly oxidizes CH_4 adsorbed on the surface of Cu in zirconia.

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Needle-type organic electrochemical transistor for spatially resolved detection of dopamine

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Detection of complex biological events at the single cell level, such as release and reuptake cycles of a neurotransmitter at a synaptic contact, holds great potential for biomedical research. However, the combination of ultra-low analyte concentration and highly spatially confined and temporally resolved biochemical dynamics remains an unaddressed challenge for conventional analytical approaches. In this view, the development of miniaturized bioelectronic systems is of particular interest.

Here, we report the design of a novel electrochemical tool combining the unmatched temporal and spatial resolution of carbon nanoelectrodes (CNEs) with the amplified transducing capability of an organic electrochemical transistor (OECT) for biochemical detection at the single cell level.

The device was obtained from single and double barrel CNEs, whose fabrication was optimised to reach adequate control on the desired size and shape of the electrodes. Therefore, a thin film of organic semiconductor was electrochemically deposited on top of them, in order to create submicrometric, nanodisk-shaped gate and channel elements. The fully assembled device was characterized and showed the typical transistor behaviour upon gating. Overall, this is the first example of a needle-type OECT with cell-compatible dimensions, and we provide its proof-of-principle application for dopamine detection in biologically relevant concentration [1].

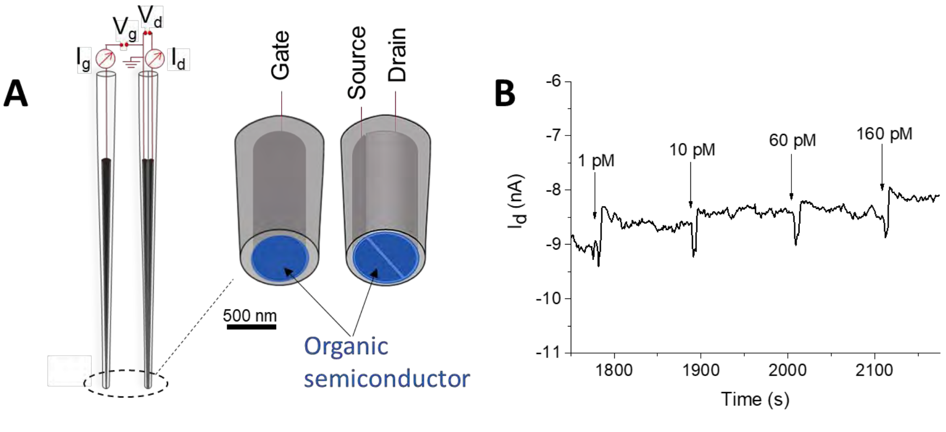

Figure 1. (**A**) Configuration of the needle-type OECT. (**B**) Current vs time curve recorded during increasing additions of Dopamine in the picomolar range ($V_g = -900$ mV; $V_d = -300$ mV).

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Carbon free membrane electrode assemblies with non – noble catalyst for AEMEC

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The AEM water electrolysis based on alkali-doped polymer electrolyte membrane is an efficient method to produce hydrogen with higher purity which offers several advantages over the traditional technologies: higher current density, low ohmic resistance, possibility to operate at higher working pressure, as well as usage of platinum free electro catalysts. The technology still has some problems such as non-sufficient stability of the polymer electrolyte at elevated temperature, low conductivity of the commercially available membranes, and intensive corrosion on the bipolar plates of the cell. This work presents a research on development of highly efficient membrane electrode assembly (MEA) with carbon free electrodes containing non-noble metal catalysts (Co and Ni supported on Magnelli phase titania), and commercially available AB-PBI anion exchange membrane. It is found that the optimal amount of the catalysts for hydrogen and oxygen evolution reactions is 1.0 mg.cm-2 and 0.5 mg.cm-2, respectively. The electrochemical performance of the prepared MEA shows low over potentials concerning both partial reactions and stable behavior at elevated temperature of 80 oC with current density of 0.6A.cm-2 at cell voltage of 2.0 V. The enhanced efficiency of the electrolysis is explained with the observed homogeneous distribution of the nano-sized catalyst crystallites on the non-carbon carrier, reduced ohmic resistance of the electrode, and high anion conductivity of the used polymer electrolyte membrane.

Acknowledgements: This work was supported by the Bulgarian Ministry of Education and Science under the National Research Programme E+: Low Carbon Energy for the Transport and Households, grant agreement D01-214/2018. Part of the experiments were performed on equipment of Research Infrastructure "Energy Storage and Hydrogen Energetics" (ESHER), included in the National Roadmap for Research Infrastructure 2017-2023", granted by the Ministry of Education and Science of Republic Bulgaria, grant agreement № DO1-160/

Voltammetric Investigation of $Th_{4-x}U_x(PO_4)_4P_2O_7$ Solid Solutions. Characterization and Effectiveness of the Uranium (IV) Entrapment

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The spent nuclear fuel consists essentially of UO_2 that is highly insoluble in reducing media, but its apparent solubility increases dramatically under oxidizing conditions (from 4 to 10 orders of magnitude) because U(IV) is transformed into soluble U(VI). Thorium phosphate-diphosphate $Th_4(PO_4)_4P_2O_7$ (TPD) was envisaged by the 'Institut de Physique Nucléaire' (IPN) of Paris-Sud University for the immobilization of actinides (Ac) [1.2]. The TPD structure allows the replacement of large amounts of Th_4^+ by U_4^+, Np_4^+ or Pu_4^+ with formation of solid solutions $Th_{4-x}\ Ac_x(PO_4)_4P_2O_7$. Several successful leaching tests have been performed with $Th_{4-x}U_x(PO_4)_4P_2O_7$ (TUPD) in very corrosive media y [3].

In this work we examine the decrease of the electro-oxidizability two of TUPD samples, TUPD10 and TUPD50, where 10% and 50%, respectively, of the Th_4^+ ions in the TPD structure were replaced by U_4^+ ions.

The electrochemical experiments were performed using the Voltammetry of MicroParticles technique (VMP) [4] where TUPD microparticles were immobilized on the cross-section of graphite electrodes. The surfaces of these electrodes were characterized by XPS and µRaman spectroscopy before and after electrooxidation. The voltammograms of Fig. 1A show that TPD is not electroactive and TUPD compounds are more difficult to oxidize than UO_2.

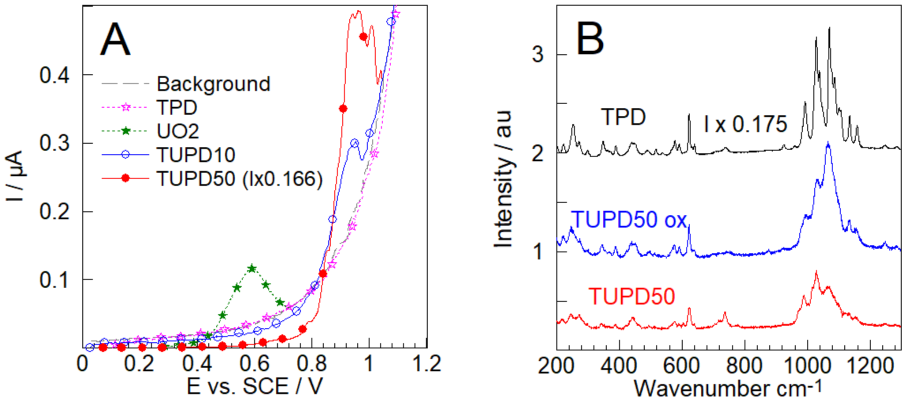

Fig. 1. (A) Voltammetric characterization of TPD, TUPD10, TUPD50 and UO_2 microparticles in 0.5 M $NaClO_4$ using VMP (scan rate 2 mV/s). (B) Raman spectra of TPD, TUPD50 and TUPD50 ox (oxidized TUPD50).

The insertion of U_4^+ ions in the TPD structure results in a significant decrease of the Raman signal (the more the U_4^+ content the less intense the signal). The electrooxidation of TUPD compounds leads to the release of about 12% of the uranium content in the case of TUPD10 and 20% in the case of TUPD50. The electrooxidized TUPD compounds are no longer electroactive and their Raman spectra become closer to that of TPD as it is shown in Fig. 1B for TUPD50.

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Application of Copolymer from Folic Acid and Riboflavin for Determination of Pesticides

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Nowadays, natural compounds in sensors are desirable. They are preferable to contribute in diminishing of climate changes and in line with the European Green Deal announced by the European Commission. Natural polymers are already used in sensor development, while polymers from natural monomers, e.g. amino acids, some vitamins or dopamine is a rather recent topic in sensing and especially biosensing [1]. Pesticides are important for a successful plant growth but they are harmful to human and animal organisms, therefore, it is important to monitor their concentration in plant products. Atrazine is a triazine class herbicide, residues of which can stay in crops or other cultivated plants.

Polymerized folic acid (PFA) or riboflavin (PRf) were already employed for detection of some compounds like glutamate, glucose and ascorbic acid [2,3]. These vitamins can be polymerized electrochemically under certain conditions [4,5]. Electrochemistry is a green synthesis method and obtained polymers from natural monomers can be used in sensors for medicine or food quality control or other biological samples.

PFA and PRf copolymer was synthesized on glassy carbon electrode in order to detect atrazine. The optimization of the copolymer composition and its electrocatalytical activity towards atrazine will be presented and discussed.

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How to Minimize Problems with Electrode Passivation in Electroanalytical Chemistry

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The possibilities of modern electroanalytical methods in environmental analysis or organic compounds are well recognized (low investment and running costs, reasonable and in many cases "fit for the purpose" sensitivity and selectivity, easy automatization, easy miniaturization resulting in portability of corresponding instrumentation, user friendliness and environmental friendliness ("green electroanalytical chemistry"). Nevertheless, the big problem connected with the use of modern electrochemical techniques in environmental analysis is the passivation of working electrodes by products/intermediates of electrochemical reactions or by components of an environmental sample which can adsorb on the electrode surface thus fouling the electrode and complicating the determination or even making it impossible. It is obvious that surface chemistry plays a deceive role in this process.

The following new approaches eliminating problems with electrode passivation in environmental monitoring of organic pollutants will be discussed and demonstrated on practical examples :

i) preparation, surface characterization and testing of new electrode materials resistant towards passivation (e.g. boron doped diamond, nitrogen-incorporated tetrahedral amorphous carbon, hydrophilic carbon prepared by pyrolysis of acetylene and hydrogenation, carbon films, nanostructured metals deposited on various substrates, bismuth and antimony films,

ii) elimination of passivation by electrochemical polishing/cleaning/pre-treatment of electrode surface between successive measurements,

iii) elimination of electrode passivation by measurements in flowing systems (liquid chromatography, flow injection analysis and batch injection analysis with electrochemical detection)

iv) prevention of passivating molecules from matrix to access the electrode surface by their preliminary separation via membrane filtration,

v) application of electrodes with easily renewable surface (dropping mercury electrode, hanging mercury drop electrode, static mercury drop electrode) and/or disposable electrodes for a single use (screen printed electrodes),

These approaches will be demonstrated on selected examples of passivating pollutants (phenols, nitrophenols, aromatic amines and nitrocompounds, dyes, drugs, etc.).

Acknowledgement
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Spectroelectrochemical properties of electrodeposited polypyrrole complexes with sulfonated polyelectrolytes

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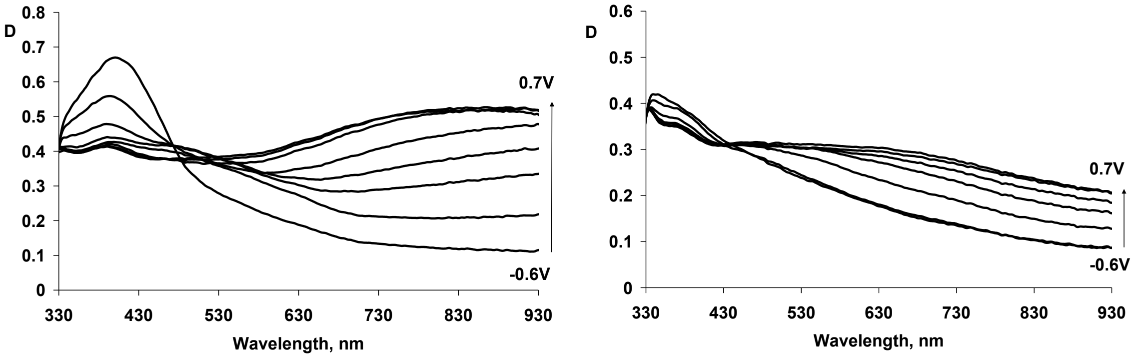
Polypyrrole (PPy) films were synthesized in galvanostatic mode in the presence of salt and acid forms of water-soluble sulfonated polyelectrolytes: flexible-chain poly(styrene-4-sulfonic acid) (PSSA) and poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPSA), semi-rigid-chain poly(4,4'-(2,2'-disulfonic acid)-diphenylene-iso-phthalamide) (i-PASA), rigid-chain poly(4,4'-(2,2'-disulfonic acid)-diphenylene-tere-phthalamide) (t-PASA).

The electronic and chemical structure of the PPy films obtained was studied by UV-Vis-NIR and Raman spectroelectrochemistry. UV-Vis-NIR spectroelectrochemical and cyclic voltammetric comparative studies were performed in water and organic (propylene carbonate) medium. It was shown that the structure of PPy depends strictly on the structure of polyelectrolyte and the nature of its cation.

In the presence of acid forms of flexible-chain polyelectrolytes PPy films are formed in protonated, more oxidized form with higher concentration of free charge carriers. PPy films electrodeposited in the presence of salt forms of all polyelectrolytes are less protonated, however they characterized by high absorption in the NIR spectral region. Their spectroelectrochemical properties are similar to those of PPy films obtained in inorganic electrolytes (Fig.1a). Contrarily, PPy complexes with rigid-chain polyacids exhibit lower doping degree, lower absorption in NIR region, which is indicative of lower concentration of free charge carriers (Fig.1b). At the same time, numerous cycling in propylene carbonate with 0.5M NaClO4 showed that films of PPy complexes with rigid-chain polyacids are more electrochemically stable.



a) b)

Fig.1 UV-Vis-NIR absorption spectra of the PPy-PSSA (a) and PPy-i-PASA (b) films at different fixed potentials in 0.1 M NaClO4 aqueous solution.

The differences are discussed considering peculiarities of pyrrole distribution in the synthesis solution depending on the hydrophobicity, conformational state and spatial distribution of sulfonic groups in polyelectrolyte coils.

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Self-organized Electrodeposition of Cu/Cu_2O towards Novel Materials

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Self-organization is a powerful tool that may be explored as a methodology for the synthesis of new materials with intricate structures. Oscillatory electrodeposition and electrodissolution reactions can enable the formation of nanostructured materials under micro and nanoscale through *bottom-up* processes.[1] The electrodeposition in an alkaline media containing copper sulfate and lactate yield periodic oscillations by only applying a constant current. The oscillations under galvanostatic regime occur in a broad range of different pH and current densities values, that directly affect the period and amplitude of the oscillations (Figure 1a).[2] Although direct relationships between experimental parameters, such as pH, current density and temperature can be obtained, multivariate statistical analysis revealed a more complex dependence on the frequency including quadratic terms (Figure 1b). The periodic oscillations related to alternate deposition of Cu and Cu/Cu_2O are recorded in the form of an ordered architecture in the electrodeposited film, the so-called multilayers. The period and amplitude of the oscillations is directly related to the thickness and composition of the layers of the electrodeposited film. Under high frequencies the thin thickness and the inhomogeneous deposition encumber the well-defined layer formation (Figure 1c), despite this, the formation of two distinct phases are clearly observed, consisting of copper oxide grains (in white) identified in Transmission Kikuchi Diffraction phase maps surrounded by a metallic copper matrix, in gray.[3] $Cu|Cu_2O$ interfaces are employed in many fields, including electrocatalysis, in the CO_2 electroreduction, in sensors, as glucose detectors, as nanowires in lithium-ion batteries, all of them who can benefit greatly from the use of new materials built through self-organized systems.

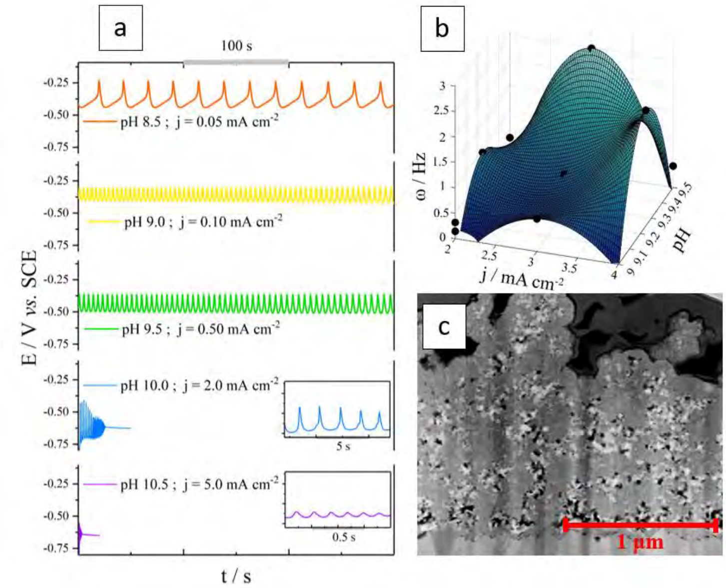

Figure 1: (a) Oscillations samples extracted from galvanostatic electrodeposition time-series with different pH values and current densities. (b) Response surface plot of the model for the Cu/Cu_2O oscillatory deposition at T = 35.0 ºC, in the pH range of 9.0 to 9.5 and current densities of 2.0 to 4.0 mA cm^{-2}. (c) High-Angle Annular Dark Field image of the cross-section lamella prepared through Focused Ion Bean (FIB) from the Cu/Cu_2O oscillatory filmed deposited over FTO substrate.

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Sodium Adsorption Ratio Reduction via Monovalent Selectivity in Capacitive Deionization with Functionalized Electrodes

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Ion-ion selectivity, the preferential removal of particular charged species in a competitive ionic environment, is an active and growing research topic in capacitive deionization (CDI) with potential water treatment applications such as heavy metal removal and agricultural water remediation[1]. We here study monovalent selectivity, the preferential removal of a monovalent ion in the presence of a divalent ion, with the aim of reducing the sodium adsorption ratio (SAR) of a test feed stream. SAR is an important agricultural water parameter, and excessive values can adversely affect plant health and reduce crop yields[2].

Using a flow-through electrodes (FTE) CDI device, we evaluate the performance of a cell with a cathode functionalized with sulfonic groups (S-P cell) for a feed water containing Na$^+$ and Ca^{2+} ions with initial SAR = 19.8 and conductivity κ = 1.75 mS/cm for a range of cycle times (6 – 30 min, equally divided into charge and discharge steps) and applied constant voltages. At cycle times of 15 and 30 min, SAR is increased above the feed value due to preferential Ca^{2+} removal. However, at a cycle time of 6 min, the S-P cell reduces SAR at voltages above 0.8 V, improving the water quality relative to the feed value (see **Figure *1***a), an effect due to greater relative removal of Na$^+$. Furthermore, we show that SAR reduction and high coulombic efficiency (>96%) are retained over a 1000-cycle experiment at 1.2 V and 6 min cycle time (**Figure *1***b), indicating the promise of functionalized electrode materials for applications involving monovalent selectivity. We discuss tradeoffs for conditions that achieve net reductions of SAR and conductivity, such as acidification of the desalinated water to pH < 6 and energy consumption of ~1 kWh/m^3 product water, the latter vs. ~0.01 kWh/m^3 for conditions that result in high Ca^{2+} selectivity.

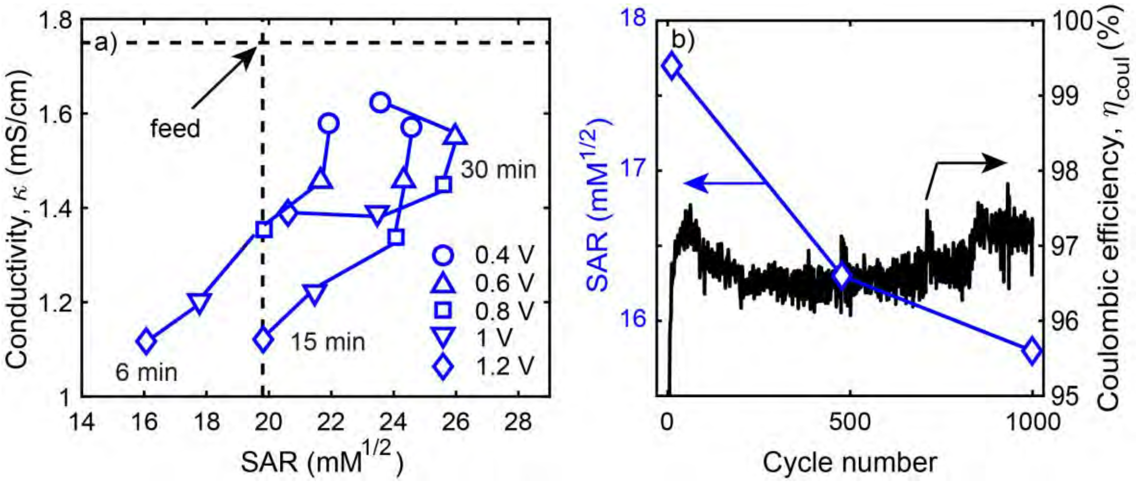

Figure 1: CDI performance in the S-P cell. a) The effect of charging voltage and cycle time on output water SAR and conductivity. Feedwater conditions are shown at the intersection of the dashed lines. b) Output water SAR and coulombic efficiency over a 1000-cycle experiment at 1.2 V and 6 min cycle time.

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Electrochemical reduction of CO_2/CO to C2+ products assisted by Cu-Ag bimetallic catalysts

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Witnessing both fossil resources scarcity and global warming consequences, it is crucial to develop sustainable answers to the rising demand in energy and chemicals. An innovative way of producing added value products for industry is to electrochemically convert carbon dioxide using electricity originating from sustainable energy sources (solar, wind, …). [1] More than mitigating greenhouse gas emission in the atmosphere, the process would allow the storage of surplus electrons produced during sunny or windy days into chemical bonds, making energy available for later use. The focus on producing long-chain compounds (C2+), having a higher energy density than one-carbon products, is a key point for further progress in CO_2/CO electroreduction (CO_2RR and CORR).

After decades of investigations, copper based electrocatalysts have proven to be active in CO_2RR towards C2+ products. [2] However, the selectivity and further improvement of the activity constitute the main challenges to overcome before any industrial applications. Despite a not fully understood reaction mechanism, carbon monoxide was shown to be the main reaction intermediate leading to C2+ products. [3] CORR focused studies have indeed been published this past decade in order to increase the selectivity towards high energy density products. [4] Knowing that CO like intermediates induce C-C coupling, some research groups [5][6] have recently investigated bimetallic system alloying copper with a CO-producing metal (e.g. Ag or Au) in order to provide localized CO production and spill over on copper domains where CO would react further. This approach enhances the CO coverage on copper and leads to increase in C-C coupling, further pulling up selectivity for C2+ compounds. Gewirth et al. [6] synthesized CuAg nanowires demonstrating a noteworthy near 100% faradaic efficiency (FE) for CO_2RR, with a 60% FE to Ethylene as well as a 25% FE for Ethanol at relatively low overpotential (-0.7V vs RHE). They also determined that half of the current density devoted to CO_2RR is directed towards Ethylene production, and one third towards Ethanol and CO formation.

These promising results constitute key knowledge for further optimization. In this work we present the study of CuAg based bimetallic systems for CO_2RR and CORR. Different electrodeposited CuAg catalysts will be presented (pure Cu, CuAg (1%at), CuAg (6%at) and CuAg (9%at)) as well as their performance in CO_2RR and CORR. Moreover, in this study we optimized the synthesis of the bimetallic catalysts by using different ligands (imidazole and triazole based) influencing the shape of the catalysts. The shape will impact the product distribution during reaction and ligands are investigated for this purpose.

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Electrocoagulation using aluminum electrodes for boron removal

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The efficiency of the electrocoagulation method in the removal of boron from synthetic effluent and mining effluent was investigated in this study. Different parameters such as pH, current density, electrocoagulation time and supporting electrolyte concentration were tested for both types of effluents [1]. The synthetic effluent was prepared from boric acid solution and the mining effluent was collected from an important brazilian mining company located in Vitória city. The results showed a percentage of boron removal higher than 60% for the synthetic effluent and close to 70% for the mining effluent, using aluminum electrodes, pH 7.5, a current density of 14.82 mA cm^{-2} and electrolyte support 0.200 mol L^{-1}. The methods of electrocoagulation and chemical coagulation were also compared in this study, where a percentage of 56.30% higher was obtained by electrocoagulation for the mining effluent. Thus, electrocoagulation was more efficient at removing boron, especially when appropriate parameters were applied. Thus, electrocoagulation proved to be an important technique for the removal of residues in industrial effluents and, consequently, a reduction of the environmental impacts caused by them [1].

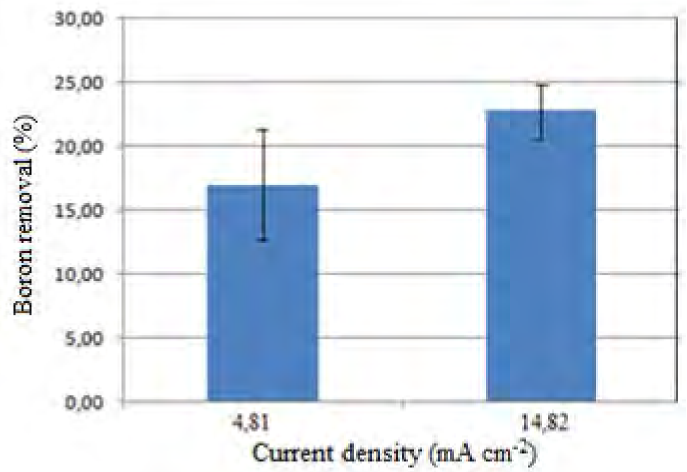

Figure 1. Percentage of boron removal at the current densities of 4.81 and 14.42 mA cm^{-2}, with a time of EC of 30 minutes and supporting electrolyte of 0.200 mol L^{-1}.

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Preparation and properties of a versatile gel polymer electrolyte for safer high voltage lithium batteries

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The introduction of a polymeric electrolyte component in lithium batteries has dramatically increased safety of these energy storage devices, thus enhancing their employment in many commercial applications. In this context the electrical conduction is one of the most important features for the choice of a suitable polymer, together with good mechanical strength and chemical stability. Hence, polymeric electrolytes can be divided in two major classes depending on their features: dry solid polymer electrolytes (SPE), where the polymeric matrix acts as solid solvent, and gel polymer electrolytes (GPE), composed of organic solvents mixed together with an appropriate polymer [1]. In both cases polymer chains take part to lithium cation diffusion through the electrolyte, improving safety but slightly reducing its ion conduction respect to liquid systems.

This work is focused on the development of a versatile GPE for high voltage lithium batteries [2], enhancing safety of the device without undermining its electrochemical performances. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) copolymer is used as polymeric component, dissolved in a mixture of alkyl carbonate solvents with an easy room atmosphere procedure for the accomplishment of a dried separator with controlled thickness. Thermal characterization of the polymeric separator is carried out with thermogravimetric analysis (TGA), differential scanning calorimetry (DSC). The membrane is then stored under inert atmosphere, ready to be swollen in liquid electrolyte solutions to form a suitable GPE. The adaptability of the separator to electrolyte solutions of different nature is demonstrated with a liquid commercial electrolyte and innovative solutions obtained with the addition of the ionic liquid N-n-butyl-N-methylpyrrolidinium hexafluorophosphate ($Py_{14}PF_6$) [3]. Pulsed field gradient NMR measurements are performed to investigate GPEs lithium diffusion coefficients and relaxation phenomena, useful for the comprehension of the ion-conduction mechanisms [4]. GPEs are also characterized by rheological and electrochemical measurements, adopting a nickel-substituted manganese spinel $LiNi_{0.5}Mn_{1.5}O_4$ as high voltage cathode in lithium metal batteries. Enhanced safety of the polymeric matrix is demonstrated with flame tests on both GPEs and their liquid counterparts.

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Graphene–ionic liquid interfacial potential drop from DFT-MD simulations

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Ionic liquids (IL) are organic salts with remarkable stability and high charge density. These properties make them promising electrolytes for electrochemical applications such as supercapacitors. As the microscopic processes taking place at the interface affect the macroscopic characteristics of supercapacitors, molecular dynamics (MD) simulations are essential to study the electrode–IL interface structure and dynamics.

In this work, we have used density functional theory-based molecular dynamics (DFT-MD) simulations to explore the interface between graphene electrode and 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid at different graphene surface charges. DFT-MD level of theory allowed us to examine the charge distribution and polarization on the graphene. The results indicate that overscreening is preserved upon the inclusion of quantum effects. Furthermore, we have divided the electrical double layer potential drop into two components to narrow the gap between classical and DFT-based MD simulations. The first involves atomic charges and arises due to the reorganization of the ionic liquid. The second quantifies the redistribution of the graphene electron density using atomic dipoles that correlate with the atomic charges. The latter term we have related to the concepts of Thomas–Fermi screening length, effective surface charge plane and quantum capacitance.

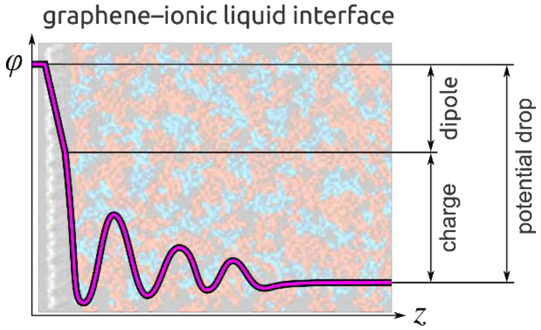

Figure 1. Interfacial potential drop disassembled into two main components arising from atomic charges and dipoles.

Acknowledgements: This research was supported by the Estonian Research Council (grants IUT20-13, PSG249, and PUT1107), the EU through the European Regional Development Fund (TK141 “Advanced materials and high-technology devices for energy recuperation systems”), and the Estonian–French cooperation program Parrot, funded by the Estonian Research Council and Campus France.

Long-term demonstration of a bioelectrochemical power-to-gas prototype, run in different operation conditions

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Bioelectrochemical power-to-gas represents a novel solution for electrical energy storage. It allows converting electrical energy to methane (CH_4), therefore connecting the electricity and natural gas grids for a high-capacity and flexible energy storage. The technology can be coupled with membrane contactors for CO_2 capture, dissolving the CO_2 in wastewater before its feeding to the bioelectrochemical system. This way, the integrated system can achieve also carbon capture, in the scenario of a wastewater treatment plant application. In this study, such technology was developed in a medium-scale prototype of 32 L (Figure 1), operated for 400 days in different conditions of temperature, voltage and CO_2 capture [1]

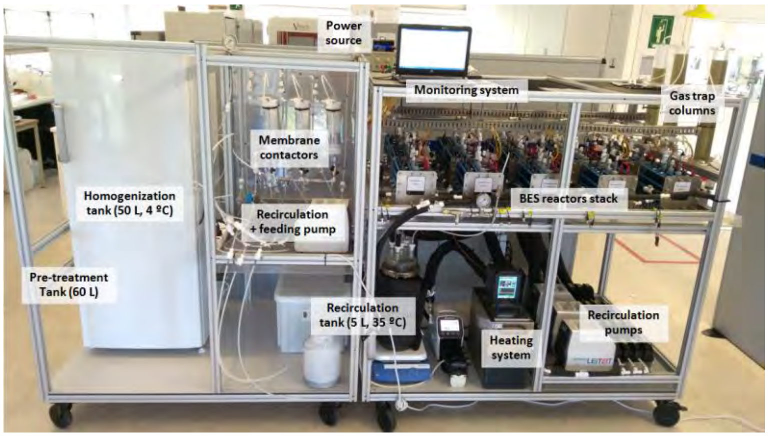

Figure 1 – Photo of developed prototype. Left side: CO_2 capture system. Right side: EMG-BES stack.

The prototype achieved the highest CH4 production rate (147±33 L m-3 d-1) at the lowest specific energy consumption (1,0±0,3 kWh m-3 CH_4) when operated at 25 ºC and applying a voltage of 0,7 V, while capturing and converting 22 L m-3 d-1 of CO_2 (Figure 2).

Traces of H_2 in the biogas, detectable during the periods of closed electrical circuit operation, indicated that hydrogenotrophic electromethanogenesis was taking place at the cathode. On the other hand, a relevant CH_4 production during periods of open electrical circuit operation confirmed the presence of acetoclastic methanogenic microorganisms in the microbial community, which was dominated by the archaeal genus Methanothrix (Euryarcheota). Different OTUs (operational taxonomic units) belonging to the bacterial Synergistes phylum were found at the anode and the cathode, having a potential role in organic matter degradation and H2 production, respectively.

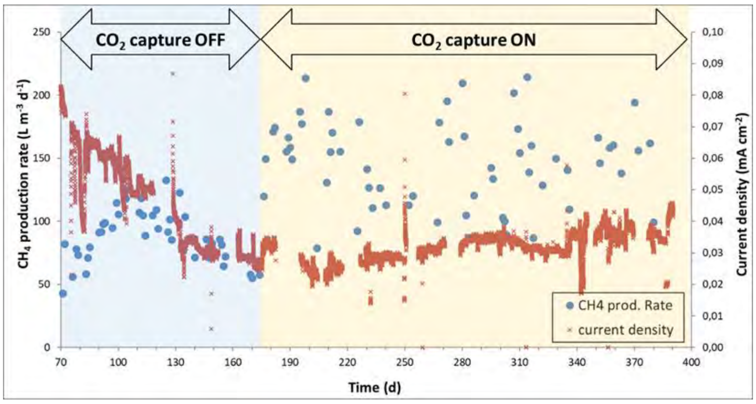

Figure 2 – Trend in time of CH_4 production rate, with and without CO_2 capture.

In the panorama of methanation technologies currently available for power-to-gas, performance of this EMG-BES prototype is not yet competitive, especially in terms of volumetric CH_4 production rate and power density demand. However, the possibility to obtain a high-quality biogas (almost respecting the quality standards of biomethane) at a minimal energy consumption represents a potentially favorable business scenario for this technology. This work has been financially supported by the Spanish Ministry of Economy and Competitiveness under the project Power2Biomethane (RTC-2016-5024-3, 2016).

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Her Activity of Nickel Coated Graphite Electrodes Doped with CoW Nanoparticles

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ABSTRACT

Hydrogen is a renewable secondary energy source. Due to its high energy density and zero emissions, it has been accepted as a suitable alternative for conventional fossil fuels [1]. Environmentally friendly energy sources for sustainable renewable resources are of interest due to the rise in global pollution. Hydrogen, seen as the energy source of the future, can be obtained in different ways. However, the most suitable method is to obtain hydrogen by electrolysis. The electrical energy used in this method increases the unit price of H_2. In addition, it increases the unit price even more because it requires additional energy in over-potential consisting of electrodes and electrolytes. In order to overcome these problems, suitable electrode, working environment and catalyst are investigated [2, 3].

In this study, the hydrogen evolution reaction (HER) effect of CoW nanoparticles deposited on the Ni plated graphite eletrodes (CoWNi@C) were studied. The HER activity of the prepared electrodes were investigated by electrochemical techniques. Electrochemical analyses were carried out by the potentiodynamic polarization techniques and electrochemical impedance spectroscopy (EIS). Surface morphology and chemical composition of synthesized nanoparticles were investigated by scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) techniques. The cathodic polarization curves of Ni @C and CoWNi@C in 1 M KOH solutions are given in Fig. 1. The addition of a small amount of CoW to the coatings in order to increase the catalytic activity led to significant differences in current densities. When current density values are compared as an expression of catalytic activity, it is seen that the CoWNi@C catalyst has higher activity than the Ni@C catalyst. It showed that HER efficacy of CoWNi@C catalyst in 1.0 M KOH solution was higher than Ni@C catalyst and showed lower potential.

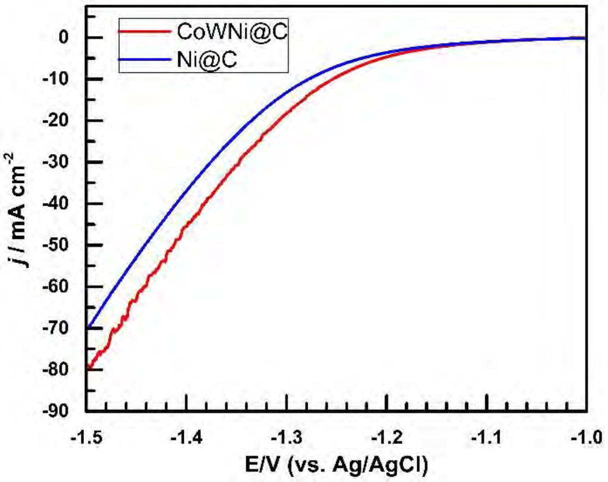

Fig. 1 The cathodic polarization curves for C, Ni@C and CoWNi@C catalysts in 1 M KOH.

Acknowledgement
We are greatly thankful to Scientific Research Project of Cukurova University (Project No: FYL-2019-12494) and CUMERLAB.

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Electrochemical Surface-Enhanced Raman Spectroscopic Study of *p*-Bromide Nitrobenzene on AgNPs@Ag Electrode

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Identification of the intermediates on the electrode-molecule surface is significant for understanding electrochemical reaction mechanisms. Surface-enhanced Raman spectroscopy (SERS) is a powerful *in situ* technique to get the molecular fingerprint information of interface reactions.[1] During the electroreduction of *p*-bromonitrobenzene (pBNB) under $NaClO_4$ aqueous electrolyte, structural transformations of surface molecules have been investigated by *in-situ* electrochemical SERS in this work.

Figure 1a shows the cyclic voltammetry of pBNB from 0.1 to -1.22 V vs. Ag|AgCl. Two cathodic waves for the nitro group reduction are observed both on the first and second cycles (red and blue curves, respectively). A pair small redox waves can be observed at -0.21 V and -0.23 V in the second CV cycle. This is similar to nitrobenzene reduction, which is identified as the redox of hydroxylamine and nitroso intermediates.[2] However, there is lack of evidence of the molecular transformation. Figure 1b presents the potenital-dependent SERS spectra in the 600-1800 cm^{-1} region. The initial spectrum of pBNB observed at 0.1 V has the typical band at 1350 cm^{-1}, which is from the nitro group. When sweeping the potential to negative potential, this results significant change in SERS. New peaks at 1168, 1339, 1386 cm^{-1} appeared in -0.4 V correspond to the reduction intermediate nitroso derivative. These bands disappear at -1 V and the SERS bands at 819 and 993 appear to prove the reduction to amino derivatives. Finally, the SERS bands at 987, 1061, 1134, and 1224 cm^{-1} can be identified as the intermediate product hydroxylamine derivative when the potenital was applied in the reversed sweep to -0.2 V.

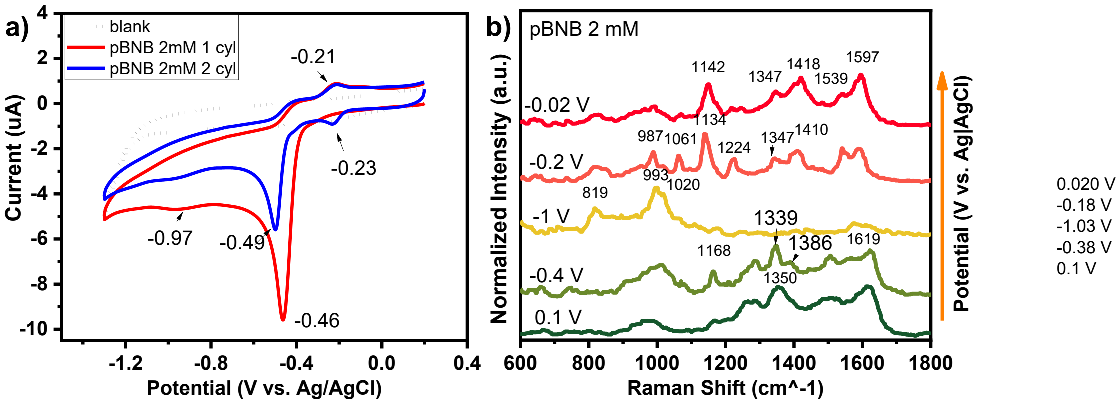

Figure 1 (a) Cyclic Voltammetry (CV) of 2 mM pBNB recorded at a scan rate of 0.1 V/s on Ag electrode. Dashed line is the first scan circle, and solid line(red) is the second circle, blank is shown in black dash line. (b) Sequence of EC-SERS at representative potentials for the reduction of pBNB obtained during CV at scan rate of 0.05 mV/s, at Ag NPs@Ag electrode. SERS spectra conditions: The integration time is 1 s. the laser wavelength 532 nm, and laser power is 150 µW, the 10×, N_A=0.3. All experiments were recorded in 2 mM pBNB under 0.1 M $NaClO_4$ solution. The reference electrode is Ag|AgCl, the counter electrode is Pt.

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Determination of Aluminum stripping & plating kinetics parameters in EMimCl/AlCl$_3$ by pulsed voltammetry for Al-ion battery

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The development of alternative battery systems that rely on cheap, non toxic, easy to recycle and worldwide available materials is of great importance for supplying huge energy storage market. One very promising candidate is the Aluminum-ion battery (AIB) that uses Graphite as intercalation material for positive electrode and an Aluminum foil or foam as negative electrode[1]. To overcome aluminium passivation and H_2 evolution, most common AIB chemistry relies of water-free ionic liquid electrolyte such as EMimCl/AlCl$_3$ mixture. During charging, large AlCl$_4^-$ anions intercalate in graphene sheets and Al is plated on the anode according to following reactions:

$$C_n + AlCl_4^- \rightarrow [C_nAlCl_4] + e^-$$

$$4\,Al_2Cl_7^- + 3^- \rightarrow Al^0 + 7\,AlCl_4^-$$

During discharging step, Al stripping occurs while AlCl$_4^-$ ions de-intercalate from graphite matrix. One crucial issue is related to graphite volume change during cycling. While a few articles report on kinetics of Al dissolution step [2,3], not information about Al deposition kinetics in ionic liquid was published yet. Herein kinetics parameter of both Al stripping & plating from/on an Aluminum foil in different EMimCl/AlCl$_3$ concentrations were evaluated by using cyclic voltammetry and high-resolution pulsed chronopotentiometry. The Tafel slopes of Al-stripping & plating were found to be in the range of 120 – 150 mV dec^{-1} while corresponding exchange current densities accounted for about 3 – 5 mA cm^{-2}. Experiments on determination of activation energy will be presented as well.

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Mesoscopic Effects in Electrocatalysis: from Concept to Catalyst Synthesis and Performance Evaluation

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In the last decade the interest in electrocatalyst design has been boosted by the increasing availability of regenerative energy in the form of electricity. The intermittent nature of energy sources such as photovoltaic power and wind energy requires suitable energy storage technology to be able to align the *"production"* with the *"demand"* of energy. While battery technology for mobile applications shows continuous progress, the storage and re-conversion of electricity in the form of energy carriers such as hydrogen gas still faces significant challenges. Complementing strategies to utilize renewable energy for the production of gases, liquids or chemicals of interest, summarized under the *"Power to value"* or *"Power2X"* label, are even more in their technological infancy. However, for an efficient regenerative energy management on a global scale such technologies are indispensable.

For all these technologies a fundamental understanding and rational design of (electro-)catalysts, on which many surface reactions of interest take place, play an essential role. In state-of-the-art academic electrocatalyst design, the focus is on optimizing the surface structure of the catalyst on a nanometer scale. This design principle, however, only takes kinetic factors into account – which are important, but not sufficient for catalytic applications. Furthermore, the electrocatalyst performance is determined at significant lower reaction rates than required for applications.

I will present our research concept that focuses on a different, complementary design approach for supported electrocatalysts in order to optimize their properties. In supported electrocatalysts, the active phase consists of metal or alloy nanoparticles distributed over a conducting support, mostly carbon based. Our aim is to elucidate *the role of mesoscopic properties* – such as the interparticle distance on the support – for their performance in a comprehensive and systematic manner by combining electrochemical measurements with (ex-situ and in operando) spectroscopy and microscopy. Mesoscopic properties have so far received only little attention in academic electrocatalyst design, yet some few studies demonstrate that they bear significant potential for improving the electrocatalyst performance. A proof of concept has been our pioneering work on the particle proximity effect on size-selected Pt clusters[1]. Different colloidal catalyst synthesis strategies[2, 3] developed allow the investigation of mesoscopic effects with a significantly broader perspective.

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Electrochromic performance of V_2O_5 thin films grown by spray pyrolysis

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Experimental results are presented related to the electrochromic behavior of vanadium pentoxide (V_2O_5) thin films deposited with a custom-made spray pyrolysis system using ammonium metavanadate as precursor. The effect of precursor concentration, deposition time and annealing on the basic characteristics of the films and their functionality was investigated in details. The films were found to exhibit quite good electrochromic behavior with four main color changes (light brown, light blue, light green and yellow). Annealed films were more stable exhibiting faster response time and larger change in the transmission between the colored and the bleached phase. These results concern a preliminary study, aiming in the development of efficient electrochromic layers using low cost and simple materials, low cost and easily adapted to a production line deposition technique, offering the possibility of developing large scale windows.

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Tailored electrocatalytic properties of Pt nanocrystals on N-functionalized carbon surface

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ABSTRACT

Pt-based nanocrystals have been largely studied due to their high activity and stability as electrocatalysts in fuel cell and water electrolyzer. For optimal electrocatalytic performance, adsorption properties of the Pt surface should be tailored toward the sweet spot where the turn over frequency is maximized while surface coverage of spectator ions is minimized. Traditionally, various approaches have been suggested with nano-architecture of Pt-based nanocrystals, including control over size, alloy composition, morphology, and surface dopants. However, there have been limited studies on the impact of carbon support surface on the adsorption properties of Pt nanocrystals. In this study, we report an unexpected change in adsorption behaviors of Pt surface when supported on the N-functionalized carbon surface. Affinity toward both protons and oxygen species are highly modulated, resulting in tailored electrocatalytic properties in acidic and alkaline electrolytes. This study will suggest the importance of carbon surface as another factor toward tailoring the performance of nano-particulate electrocatalysts.

Carbon nanofibers doped with metals for air-cathodes. Oxygen reduction reaction characterization and application in microbial desalination cells

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Bioelectrochemical Systems (BES) are novel technologies using microorganisms to catalyse different electrochemical processes. Among BES applications, Microbial Desalination Cell (MDC) (Figure 1) constitutes an emerging energy efficient desalination technology. The main advantage of MDC is lower energy required to drive desalination process (potentially 0.5 $kWhm^{-3}$) compared to reverse osmosis (3 $kWhm^{-3}$). MDC performance depends on the performance of key components (anode, cathode and membranes). In the present study, air-cathodes, based on carbon nanofibers (CNFs) doped with metal nanoparticles (Fe and Co), were developed using electrospinning. Oxygen reduction reaction (ORR) kinetics were assessed by chronopotentiometry, cyclic voltammetry and OCV.[1] CNFs demonstrate suitable ORR performance which is essential for use as air-cathode-MDC electrodes. CNFs incorporating Fe nanoparticles further enhanced ORR. Finally, an air-cathode-MDC reactor was constructed with optimized electrodes, observing high relationship between material ORR performance and desalination rate. Developed cathodes are an alternative to Pt-based cathodes and are suitable to be used in others BES and electrochemical technologies. Research leading to these results has received funding from EU-Horizon 2020 programme. GA Nº685793 (MIDES project).

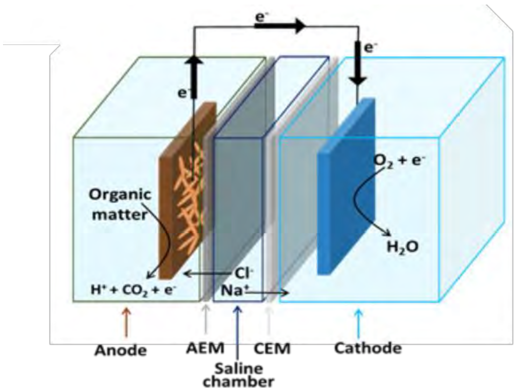

Figure 1: Structure of a Microbial Desalination Cell (MDC).

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Molybdenum selenide/sulfide with carbon nanotubes as attractive electrode materials for electrochemical capacitors

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Electrochemical capacitors (ECs) are considered to be the most promising high-power energy storage devices for various application including portable electronics, hybrid vehicles or communications due to their stable long-life cycle and high specific capacitance. Carbon materials such as activated carbons, carbon nanotubes or carbon fibres are the most common electrode components used in ECs. Although, while constructed in ECs cells in comparison to other materials, they offer relatively small specific capacitance due to limited specific surface area or non-uniform distribution of pores.

Among various electrode materials, 2D transition metal dichalcogenides (2D-TMDs) are interesting choice due to their two dimensionality, large specific surface area and large diversity of compounds. TMDs are layered material with a formula of MX_2, where M is the metal atom, e.g., Mo, V, Re etc. and X is the chalcogen atom, e.g., S, Se or Te. Atoms are bonded with each other by strong covalent bond and layers are stacked together with weak van der Waals forces. While assembled in ECs, 2D-TMDs can store charge through adsorption of ions at the electrolyte/electrode interface and also through faradaic reactions occurring on the surface of the electrode. Their structure can be tailored to obtain high specific surface area which will ensure the space for adsorption of ions and active sites for faradaic reactions [1].

$MoSe_2$ as a representative of 2D-TMDs is a semiconductor which gained significant attention due to a high theoretical capacity and a low cost. It possesses slightly higher intrinsic electrical conductivity than MoS_2 mainly due to the metallic nature of the Se. Additionally, unsaturated Se edges possess stable structure and can occur in multiple electrochemically active sites which is a beneficial for the faradaic capacity and decrease the internal resistance. $MoSe_2$ as a mainly pseudocapacitive material suffers from poor electrical conductivity which in total decreases the overall electrochemical performance [2].

It was already proven that multiwalled carbon nanotubes (MWCNTs) show superior electrical conductivity and could serve as a good percolator of various electrode materials in ECs. Combination of highly conductive MWCNTs with faradaic $MoSe_2$ resulted in obtaining stable, highly capacitive composite with improved conductivity. Moreover, the addition of MWNCTs increased the overall lifespan as they prevent the $MoSe_2$ from volume expansion during charge/discharge which has its origin in more metallic nature of Se. Several $MoSe_2$/MWCNTs composites with various composition were prepared by simple hydrothermal method. For comparison MoS_2/MWNTs composites have also been prepared. The obtained composites were characterized with various textural/structural methods, e.g., scanning electron microscopy, X-ray diffraction and Raman spectroscopy. The electrochemical performance of the prepared ECs cells were studied by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. Two- and three-electrode cells were tested. Neutral aqueous solutions (sulfates) have been selected as electrolytes to extend operational voltage of EC.

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PElectrogenerated Chemiluminescence and Photophysical Properties of Oxazaborines Molecules

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An important and novel group of fluorophores that are tetra-coordinated six-membered boron compounds with O- B- N moiety, are called Oxazaborines (Figure 1b). These molecules have ignited great interest to be investigated due to their aggregation-included emission and for obtaining the forming donor-acceptor (D-A) chromophores.[1] The investigation of Oxazaborines' properties yield a high photoluminescence (PL) of 70-75% which is relative to their first redox behavior. The use of the electrochemiluminescence (ECL) method demonstrates the high ECL intensity which has a value four times higher than the standard dyes, therefore opening novel applications within the ECL luminophores field (Figure 1a).[2][3] Finally, all of these novel compounds were analyzed under the same conditions, in order to make it possible to create a comparison between them. Thus, the ECL analysis of the above compounds was carried out in an aprotic solvent.[4]

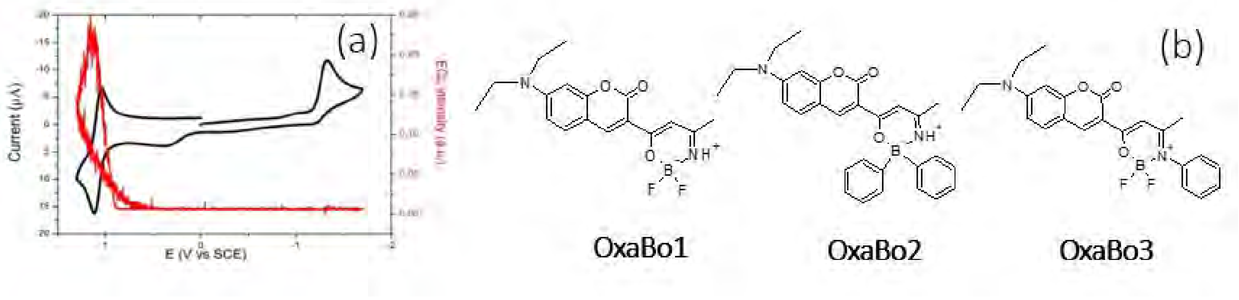

Figure 1: (a) ECL intensity vs potential for 5.10^{-4} M OxaBo3 (current in black and ECL in red) in CH_3CN/Bu_4NPF_6 (0.1 M). Working electrode: Pt disk (2 mm diameter) vs SCE electrode with scan rate 1 Vs 1. PMT bias of 750 V; voltage scan between +1.3 and -1.7. (b) The structures of Oxazaborines

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Cysteine detection at mesoporous Silica Films functionalized with Ferrocene

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Cysteine is a thiol containing semi-essential amino acid which plays an important role in cellular functionality to counter oxidative stress in living cells [1]. It also has a role in certain cell signaling pathways [2] and regulatory functions [3]. Since, the cysteine amino acid is a part of glutathione tripeptide, selective detection of cysteine over glutathione always remains a challenge.

Herein, we report a novel strategy for the selective detection of micromolar concentrations of cysteine over glutathione, taking advantage of the electrocatalytic properties of ferrocene in the electrochemical oxidation of cysteine [4]. Ferrocene functionalized mesoporous silica films have been used for this purpose (Figure 1).

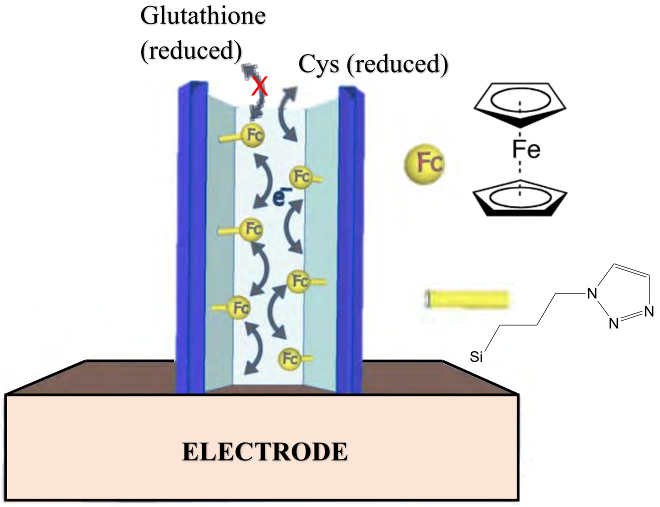

Figure 1: Selective oxidation of cysteine over glutathione and electron hopping effect in the ferrocene functionalized silica film

The films were prepared by electrochemically assisted self-assembly (EASA) method followed by copper-catalysed azide-alkyne Huisgen cycloaddition reaction [5]. Vertically aligned mesoporous silica films display good selectivity [6] and sensitivity [7]. The pores of the films are ~2 nm in diameter and offer a highly selective surface for small molecules. These ferrocene functionalized films were characterized by cyclic voltammetry and show good electrocatalytic activity for the oxidation of cysteine [8]. Further, we also discuss the electron transfer kinetics for such an electrocatalytic reaction and the effect of diffusion of molecules in the 1D mesochannels of mesoporous films. In order to improve the detection sensitivity, flow injection amperometry has been performed and is used for selective detection of cysteine in the concentration range from 3 to 100 µM in buffer solution.

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Friction at electrode surface: Effect of adsorbates and potential

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Friction between sliding AFM tip and the surface of electrode in contact help us to understand interfacial and tribological behavior on nanoscale. The measurement of friction in an electrochemical cell allows controlling the interfacial interactions in situ easily. Our interest has been focused on the adsorption of foreign metals, ranging from (sub)monolayer (underpotential deposition(UPD)) to multilayer (bulk deposition) and the adsorption of organic adsorbate depending on a potential on single crystal electrodes in aqueous electrolyte[1-3]. In addition to studies made in aqueous electrolyte, ionic liquids have been introduced for friction study to investigate their structures depending on a potential.[4, 5].

In this study, we investigate the interfacial properties on Au(111) in aqueous electrolyte. The structure of Ag UPD layers is extremely sensitive to co-adsorbed anions such as ClO_4^-, I^- and SO_4^{2-}. In perchlorate electrolyte, Ag UPD layers show different structure depending on the existence or nonexistence of the iodine adlyer on Au(111)[6,7]. We found that the iodine adlayer on Au(111) forms a $(\surd 3\times\surd 3)R30°$ structure using the results of atomic stick-slip. It changes to a $p(3\times3)$ and $(\surd 3\times\surd 3)R30°$ structure after 1st Ag UPD and 3rd Ag UPD, respectively. The results of the friction on potential shows that the incomplete Ag UPD layer on Au(111) leads to relatively high friction. It is in good agreement that for low and moderate coverages, the tip drags the adsorbates along the surface resulting in high friction, whereas for higher coverages the tip slides above the adsorbates resulting in low friction[6]. The results of the friction on load on I-modified Au(111) shows three apparent regimes. Under the low normal load (F_N<30nN), the friction force is independent on Ag UPD, meaning that the tip is interacting with iodine layer. Under critical normal load, the friction shows a rapid increase, which indicates that the tip penetrates into the iodine layer. Under the high normal load (F_N>100), the friction shows moderate increase, which represents that the tip is interacting with Ag UPD layer.

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Revealing the mechanism of the performance discrepancy between Li and Na metal anodes

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Lithium and sodium metal anodes are promising candidates for next-generation energy storage systems because of the high theoretical capacity and low working potentials. It is reported that the high affinity between Li/Na metals and the electrodes can help suppress the dendrite growth and thus improve the reversibility of Li/Na plating/stripping cycles.[1-3] However, we find that the average Coulombic efficiency and lifespan for Na is superior to that of Li in literatures (Figure 1a). Therefore, we systematically investigate the fundamental electrochemical behaviors and interphase chemistry of Li and Na metal anodes. We uncover that the reversibility difference is correlated with the plating geometry, which originates from the concentration polarization at the interphase between Li/Na metal and the electrolytes (Figure 1b, c).[4] More importantly, we propose ways to ameliorate the reversibility of Li metal anodes. We believe the work can shed light on the researchers for the understanding of Li and Na metal anodes and further designing high-performance Li and Na metal battery.

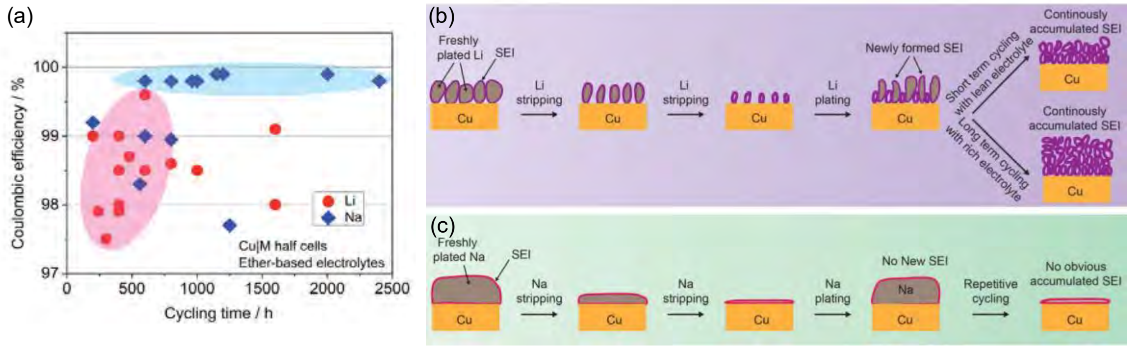

Figure 1. (a). Summary of coulombic efficiencies and cycling time of the Li and Na plating/stripping cycles reported in the literature. The scheme of the cycling process of (b) Li and (c) Na metal anode.

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Fabrication and Characterization of Electrodeposited Nickel-Graphene Oxide Composite Coating on Mild Steel for Corrosion Protection

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Nickel-based composite coatings have been used widely in various industries due to its good corrosion protection ability and graphene-oxide have attracted enormous interest due to its wide range of properties, such as excellent mechanical properties, impermeability, chemical stability and thermal stability. In the present work, we have fabricated nickel -graphene oxide (Ni-GO) composite coating on mild steel substrate by facile and cost-effective electrodeposition techniques, and characterized by XRD, FE-SEM, and EDX. XRD analysis shows that the growth of Ni-GO coating is along the 111 and 200 planes. FE-SEM image indicates the enhancement in the compactness of the coating and EDX confirmed the successful incorporation of the carbon content in the Ni-GO coating. Further, electrochemical polarization test and electrochemical impedance spectroscopy are carried out to study the corrosion resistance of the coating in 3.5% NaCl solution. The effect of various current densities (10, 20, 30, 40, 50 mA/cm^2) on the morphology and corrosion protection properties on the coating is also investigated and discussed in detail. The corrosion rate is found to be lowest at the current density of 40 mA/ cm^2 due to its better compactness of Ni-GO coating. Moreover, immersion test is also performed for three days where the corrosion rate of composite coating is reduced as compared to bare steel. This work finds a new way to fabricate GO-based composite coating on mild steel for effective corrosion protection.

Catalytically Active Re-Ni and Ni-Re-P Coatings as Electrocatalytic Materials for Hydrogen Evolution Reaction

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Electroplating and electroless chemical deposition are used for formation of catalytically active Re–Ni coatings. Re–Ni deposits prepared by electrodeposition contain 55–88 at. % of rhenium. It is found that these coatings have an amorphous structure and contain metallic nickel and both metallic and oxides forms of rhenium. The oxidized forms of rhenium are obviously oxides containing rhenium in the intermediate oxidation states. Re–Ni cathodes demonstrate high catalytic activity in 1.0 M sodium hydroxide solution. The logarithm of exchange current density of the hydrogen evolution reaction (HER) for the most catalytically active Re–Ni alloys containing 80 at.% of rhenium is –3.4. The obtained materials are stable in alkali solutions under electrolysis conditions, but they are unstable in acidic media.

On the contrary, Ni–Re–P coatings obtained by electroless deposition using sodium hypophosphite as a reducing agent are promising candidates for HER electrocatalysis in acidic solutions. The deposits are also X-ray amorphous and contain metallic rhenium, metallic and oxidized forms of nickel, and some phosphorus.

Therefore, Re–Ni coatings prepared by electrodeposition are promising for electrocatalysis of HER in alkaline solutions, whereas Ni–Re–P deposits obtained by electroless deposition are attractive candidates for hydrogen evolution in acidic solutions.

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Self-supported NiFeP layer coated nickel phosphide rods as bifunctional water splitting electrocatalyst in alkaline solution

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Developing nonprecious metal, efficient and stable electrocatalysts is still a big challenge for industrial water electrolysis to produce hydrogen and oxygen gas. Elemental doping to modulate electronic structure, and morphology engineering have proven to be effective for enhancing materials' catalytic activity. In this work, we report a facile and practical method to fabricate self-supported NiFeP coated nickel phosphide rods on Ni foam (NiFeP@NiP@NF) by phosphorizing NiFe Prussian blue analogues (PBAs) coated on nickel phosphate hydrate rods grown on Ni foam. The NiFeP@NiP@NF electrocatalyst shows efficient oxygen evolution activity, exhibiting low overpotentials of 225 and 252 mV at current densities of 10 and 100 mA cm^{-2}, respectively, in 1.0 M KOH. NiFeP@NiP@NF can also work as an active electrocatalyst for hydrogen evolution reaction with a low overpotential of 99 mV at a current density of 10 mA cm^{-2} in the same solution. Thus, the catalyst can act as both anode and cathode in an electrolyzer, requiring a cell voltage of 1.56 V to afford a 10 mA cm^{-2} current density. Furthermore, the composite material exhibits outstanding stability for continuous water electrolysis over 120 h. The high catalytic activity and excellent durability of this material are attributed to the synergistic effect of nickel and iron phosphide, and the core-shell rods structure. This method could be applied to prepare other bimetallic phosphide electrocatalysts with similar structure in the future.

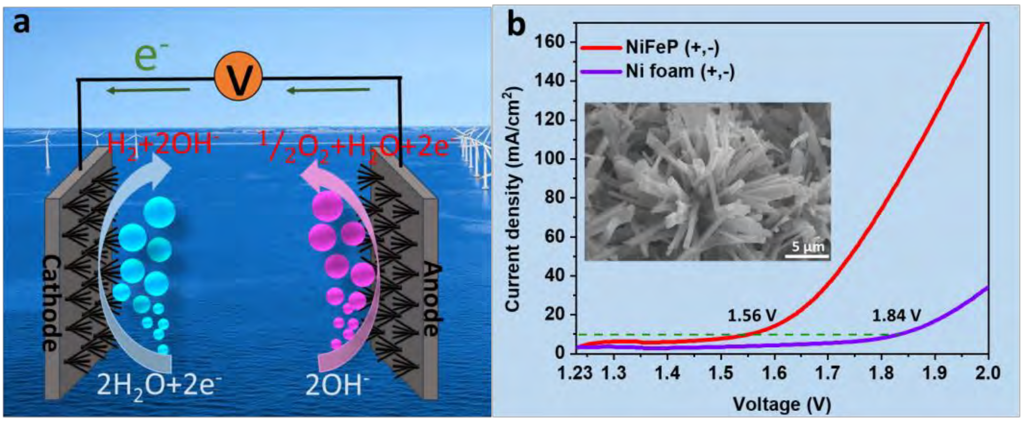

Figure 1. a. Scheme of water splitting (left). b. Polarization curves of NiFeP@NiP@Ni foam (+,-) and Ni foam (+,-) for overall water splitting in a two-electrode electrolyzer (right); Inset: SEM image of NiFeP@NiP@NF.

Thin films of molybdenum-based 2D or amorphous materials for the hydrogen evolution reaction

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Hydrogen has been considered a promise for clean and sustainable energy resource to replace the finite and traditionally fossil fuels. The water can be split into hydrogen and oxygen with the aid of electricity or solar radiation, which is a renewable and sustainable technology for hydrogen generation. A limiting factor for water splitting is the shortage of low-cost and high-efficiency catalysts. At the date, Pt provides the best hydrogen evolution reaction (HER) catalysis, but it is too expensive and scarce. Molybdenum-based materials, such as 2D-MoS_2 and amorphous MoX (X= S or O), is pointed out as favorable alternative to the Pt HER catalysts. In this work, we have investigated the performance of molybdenum-based two-dimensional (2D) and amorphous thin films as catalyst for HER. Samples have been prepared according a methodology developed by us[1] based on a reaction between ammonium molybdate and ammonium sulfide in acidic media, directly in one phase reaction or in a liquid/liquid (L/L) interfacial system. The samples were characterized by Raman spectroscopy, X ray diffraction, scanning electron microscopy (SEM) and linear sweep voltammetry. The synthesis carried out in one phase system leads to an amorphous powder composed by molybdenum sulfide and oxide that can be easily converted to a mixture of crystalline MoS_2/MoO_3 with a proper annealing at inert atmosphere. Otherwise, the synthesis at the L/L system gives rise to a thin film of amorphous MoX directly at the L/L interface. Also, with liquid phase exfoliation in acetonitrile of the mixture between MoS_2/MoO_3 these two materials were separated, yielding a homogeneous and stable dispersion of 2D-MoS_2, which is separated from the undispersed MoO_3 by centrifugation. The dispersion was used to prepare thin films of 2D-MoS_2 based on the L/L interfacial method.[2] The deposition of the MoX and 2D-MoS_2 can be made in any kind of substrate. In order to analyze the potential of the materials for HER, the films were deposited over ITO or glassy carbon. The linear sweep voltammetry was made in H_2SO_4 0.5 mol L^{-1} as electrolyte. It was observed that the electrode plays a crucial role in the performance of HER. Both materials showed currents below 2.5 mA cm^{-2} when deposited over ITO, however a totally differently behavior was observed when the materials were deposited in glassy carbon instead, in which MoX and 2D-MoS_2 showed an overpotential of 255 mV cm^{-2} and 344 mV cm^{-2} at 10 mA cm^{-2}, respectively. The difference in the overpotentials could be addressed to the wrinkly morphology and composition of the amorphous film, which provides vacancies along the sample, that improve the catalytic behavior for HER comparable to the 2D-MoS_2, which have the active sites only in the edges. An overview of the work is presented in Figure 1. Overall, this works presented a simple, original and versatile route to prepare different molybdenum-based materials thin films and showed the potential of the materials as catalyst for hydrogen generation by water splitting.

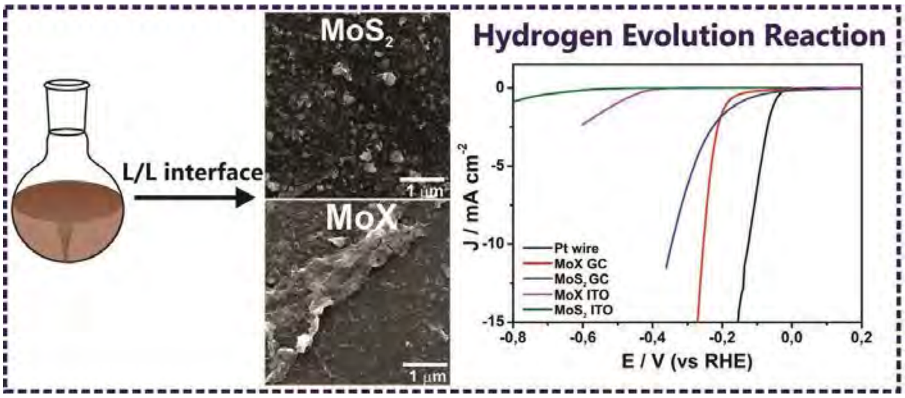

Figure 1. Summary of the materials obtained and the performance in HER.

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Biomimetic electrochemical sensor for the highly selective detection of azithromycin in biological samples

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Antibiotic resistance has a significant impact on health and therapeutic efficacy, the World Health Organization (WHO) recommending a careful monitoring of the use and disposal of this class of drugs. Therefore, there is a rising demand for highly sensitive sensors able to selectively detect low concentrations of antibiotics from different matrices in a fast and decentralized manner.

The purpose of this study was to develop an electrochemical sensor for the detection of azithromycin from various conventional (urine, plasma) and nonconventional (tears) biological fluids, by combining the convenient synthesis and analytical robustness with the tailored selectivity offered by molecular imprinting.

For molecular recognition and signal transduction a thin (~75 nm) imprinted polymeric film, using 3-thienyl boronic acid as functional monomer and 2,2´-bithiophene as crosslinker, was electropolymerized on the surface of a glassy carbon electrode. The resulting polymeric layer, both by covalent interactions (cyclic ester formation with the cis-diol moieties) and steric/functional complementarity of the imprinted cavities, is rendered highly selective towards the template molecule (azithromycin).

The surface morphology and the analytical performances of the developed sensor were assessed by scanning electron and atomic force microscopy, electrochemical impedance spectroscopy and cyclic voltammetry. By employing an indirect electrochemical detection using cyclic voltammetry in the presence of 10mM ferro/ferricyanide as redox probe, the sensor exhibited a very wide dynamic range (13.33 nM to 66.67 μM), with an estimated detection limit in the subnanomolar range (0.85 nM azithromycin). Under the optimized conditions the simple to construct sensor could be reused multiple times (>5) without significant loss in the signal intensity, has a good shelf-life (>1 month) and exhibits remarkable selectivity over a wide number of structurally related and non-related antibiotics, commonly associated drugs and endogenous compounds. The fabricated sensor was successfully applied for the quantitation of azithromycin from different biological samples (urine, plasma, tears).

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A Desalination Fuel Cell

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Desalination has evolved into a viable alternative to fresh water supply, increasing water availability and decreasing scarcity. Reverse osmosis (RO) is the most-widely used technology today for desalination, and requires significant electrical energy investment, about 4 kWh/m^3 of treated water, when desalinating sea water. In contrast to such conventional desalination systems which utilize energy, we here introduce the desalination fuel cell, which takes chemical energy as input, in the form of hydrogen and oxygen gas, and produces both desalted water and electricity simultaneously. Thus, water can be desalinated without any external electrical supply required. The desalination fuel cell is based on continuous energy conversion from chemical to electrical, and thus is not cyclic as with capacitive deionization.

As with an ED cell, our cell consists of one anion and one cation exchange membrane which sandwich a desalination channel fed with feedwater. Unlike an ED cell, on the opposite side of the anion exchange membrane is a hydrogen anode and anolyte, while an oxygen cathode and catholyte are placed opposite to the CEM. During operation, the reductant present in the anolyte (hydrogen) and oxidant present in the catholyte (oxygen) react spontaneously at the anode and cathode surfaces, respectively, providing an electric current between the anode and cathode which can be delivered to a load. The half-reactions also give rise to a spontaneous ionic current through the cell, which drives ion removal from the desalination channel[1].

The cell was characterized experimentally in single-pass mode for various catholytes and anolytes, including using feedwater as anolyte and catholyte (feedwater was 0.5 M NaCl). When using a slightly acidic catholyte (pH = 1) and basic anolyte (pH = 13), the cell demonstrated significantly higher voltages and electricity production during desalination. The results of the latter experiments are shown in Fig. 1 for varying feedwater flowrates. Fig. 1a shows polarization curve measurements that were performed. A high open circuit voltage (OCV) of ~1.6 V was reached, while the flowrate affected voltage at higher currents (~ 5 mA/cm^2). Fig. 1b shows the effluent concentration at the downstream end of the desalination compartment. We can see that at lower flowrate (0.1 ml/min), the cell performed near-complete desalination at a single pass. Furthermore, we calculated the desalination efficiency and recovery efficiency and compared it to a dedicated thermodynamic model that we developed for chemical energy driven desalination systems.

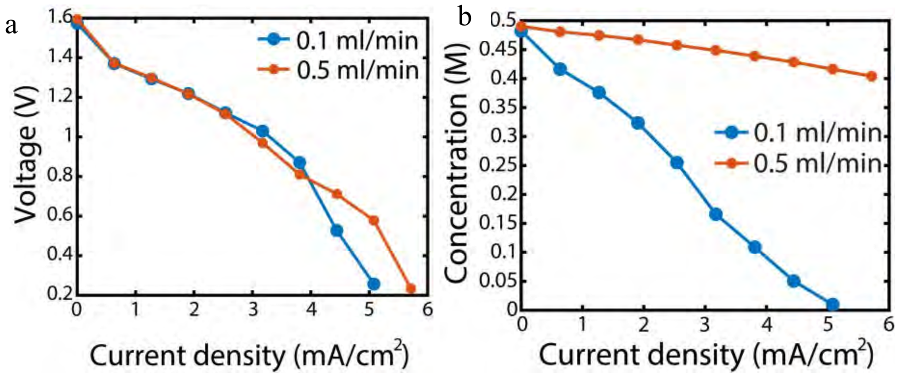

Fig. 1: Experimental results from our desalination fuel cell prototype device. a) Polarization curve measurements. b) concentration of the desalted effluent leaving the cell after a single pass.

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Development of Oxygen-Deficient $CaFe_2O_4$ Nanostructures as High-Performance Electrode Material for Pseudocapacitors

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The poor electronic/ionic conductivity and low cyclic performance of iron-based oxides hinder their practical application as electrode materials for high-performance pseudocapacitors. Owing to this, introduction of defects such as oxygen vacancies in iron-based oxides could alter their electronic/ ionic conductivity and thereby, improve the energy storage performance. Herein, we have fabricated nanoparticle and nanofibers of $CaFe_2O_4$ (CFO) by combustion and electrospinning technique, respectively, and characterized by XRD, FE-SEM, TGA, TEM, and BET. EPR and XPS reveal the presence of higher concentration of oxygen vacancies in nanofibers of CFO than their nanoparticles. The energy storage performance of CFO is further investigated by CV, GCD, and EIS. The specific capacitance of CFO nanofibers is found to be 380 (±10) F g^{-1} at 1 A g^{-1} in 3M KOH, which is higher than their nanoparticles (225 (±10) F g^{-1}). The improved performance of nanofibers of CFO is attributed to the alignment, high aspect ratio, and void/gaps present in the nanofibric architecture. These voids/ gaps are beneficial to facilitate smoother percolation of electrolyte to the interior of active electrode materials and enable high and stable capacitance. In addition to morphological features, the presence of higher concentration of oxygen vacancies in nanofibers leads to better electronic/ionic movement. This work opens a new strategy to develop Fe-based oxides as high-performance electrode materials for pseudocapacitive applications.

Comparison of In-situ ^{57}Fe Mössbauer Spectroscopic Data for Differently Prepared Fe-N-C Catalysts

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Electrochemical energy conversion in proton exchange fuel cells (PEFCs) is very promising for world-wide energy demand, especially in the transportation sector [1]. Currently, the application is hindered by the high costs of platinum-based catalysts. For the oxygen reduction reaction, Fe-N-Cs are promising to replace Pt based catalysts.

^{57}Fe Mössbauer Spectroscopy is powerful in obtaining detailed information of iron sites, with respect to structural composition, electronic states as well as magnetic environment [2-3]. The active site structures have been debates for a long time and different geometric structures have been proposed for differently prepared catalysts by multi-characterization methods, which indicate there might be indeed different active site structures from different preparation routes [4-5].

In this work, in-situ Mössbauer spectroscopy coupled with electrochemistry is used to get more insights on similarities and differences between differently prepared catalysts. The in-situ data are compared and similar trends on the active sites will be summarized for the three different catalysts. Based on this, further insights on the active site structure in Fe-N-C catalysts can be gained.

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Ion-transfer Voltammetry as a Powerful Tool in Electrochemical Investigation of Biogenic Amines

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Electrochemistry at the liquid – liquid interface, or the interface between two immiscible electrolyte solutions (ITIES) gains more and more interest among scientists due to its wide range of applications including electrochemical sensing. Detection at ITIES is not dependent on oxidation or reduction processes (common in electroanalysis) and can ensue from a simple interfacial ion transfer reaction – truly unique property [1]. Biogenic amines (BA) are biologically active compounds supplied to the human body together with food we consume. It was recognized that at elevated concentration (e.g. in some cases, 5-10 mg of histamine can lead to human poisoning) these compounds are directly related to the health risks, from light to heavy intoxication or disorder of many metabolic processes. Their increased content in food products results from microbial decarboxylation of amino acids during fermentation, processing and storage of raw materials or endogenous enzymes activity contained in raw materials. Furthermore, the presence of increased concentrations of BA can be directly related to the food spoiling. Consequently, simple and cheap methodologies have to be develop to monitor these species at different stages of food storage and processing.

Within this paper, the electrochemical behavior of selected BA at the ITIES has been studied using ion–transfer voltammetry (ITV). Voltammetric experiments were performed in the conventional four electrode macroscopic cell (macro-ITIES, see Fig. 1) using 10 mM HCl as an aqueous phase while the organic phase was the solution of hydrophobic salt dissolved in 1,2-dichloroethane. The effect of concentration of the investigated BA on the analytical signal was studied. Based on obtained results analytical parameters such as: linear dynamic ranges (LDRs), limit of detections (LODs) and sensitivities were established. Furthermore, the effect of pH on the analytical signal was tested and the results are plotted in a form of ion partition diagrams. The precision and repeatability of the method were also checked. The obtained results showed that the elaborated procedure can be successfully apply for screening purposes.

Fig. 1. Traditional macroscopic ITIES cell.

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Development of a Sandwich Molecularly Imprinted Polymer Based Sensor for Adenosine Detection

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Abnormal concentrations of adenosine, an endogenous purine with vital roles in all cells of the human system, represents a diagnostics marker of several metabolic disorders and diseases. The purpose of this study was to develop an innovative sandwich MIP-based electrochemical sensor for fast and reliable detection of adenosine in biological samples.

A novel electropolymerized sandwich molecularly imprinted polymer (MIP) was designed. The MIP film relies on the formation of covalent-imprinted biomimetic recognition sites generated by the overlapping of two polymeric layers. The first one is a boronate-affinity bithiophene layer (consisting of 2,2´-bithiophene and a boronic acid functional monomer) and an overlaying poly(3-indolacetic acid) intended to extend the selectivity towards adenosine. The selective binding of adenosine is occurring by a double recognition mechanism (IF ~ 4.5), both through functional (covalent and noncovalent) and spatial complementarity. Indirect electrochemical detection is performed in the presence of ferro/ferricyanide as redox probe. Electrochemical impedance spectroscopy and cyclic voltammetry was employed for sensor characterization, whereas differential pulse voltammetry served for the quantitative determination of adenosine. The MIP based sensor can be used multiple times without significant loss in the signal intensity, exhibiting a linear response in the range of 37.4 nM – 37.4 µM, with a LLOD of 21 nM in pH 7.4 phosphate buffer solution. The selectivity of the MIP sensor towards adenosine against other nucleosides and other relevant structurally-related interferents was also demonstrated. The developed sensor was applied for the fast and quantitative assessment of adenosine in spiked urine samples with good recoveries (102.98% - 106.34%).

This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2016-0628, within PNCDI III and by European Social Found, Human Capital Operational Programme 2014-2020, project no. POCU/380/6/13/125171.

Electrochemical and computational study of the chiral interactions of propranolol enantiomers at the surface of L-cysteine modified gold nanoparticles

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Gold nanoparticles are important components for biomedical application, offering unique optoelectronic and catalytic properties. As such, they continue to attract considerable interest in electrocatalysis and in the design of chemo- and biosensors. Cysteine can be used to control the size and shape of chemically or electrochemically obtained gold nanoparticles. By adding L-cysteine to the $HAuCl_4$ solution used for gold electrodeposition, the number of nucleation sites and overall process kinetics are improves without major changes in the purity of deposits.

The present study aimed to investigate the enantioselective interaction of a model chiral drug molecule, propranolol at the surface of L-cysteine functionalized gold nanoparticles using electrochemical techniques (differential pulse voltammetry and electrochemical impedance spectroscopy) and computational modeling (molecular dynamics simulations).

L-cysteine modified gold nanoparticles were potentiostatically (-0.4V vs. Ag/AgCl, 3M KCl) electrodeposited on the surface of a glassy carbon electrode, followed by the spontaneous adsorption of propranolol's enantiomers on the gold surface. The differences in the differential pulse voltammetric behavior of the two physisorbed enantiomers was investigated in pH 7.0 phosphate buffer.

Computational modeling served for the identification of the main attractive forces responsible of the chiral molecular interactions between the covalently bound L-amino acid and the enantiomer adsorbates. It was shown that the R(+) antipode is involved in a significantly higher number of hydrogen bonding than the S(-) antipode, being responsible of the recorded enantiospecific electrochemical signal.

Correlating electrochemical data with computational modeling allows a deeper understanding of fundamental molecular interactions occurring at the electroactive surface and may enable a more rational design of future chiral electrochemical sensing platforms.

Acknowledgement: This work was supported by a grant of Ministry of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1-TE-2016-0628, within PNCDI III and by European Social Found, Human Capital Operational Programme 2014-2020, project no. POCU/380/6/13/125171.

Development of alginate based hydrogel for supercapacitors electrolytes

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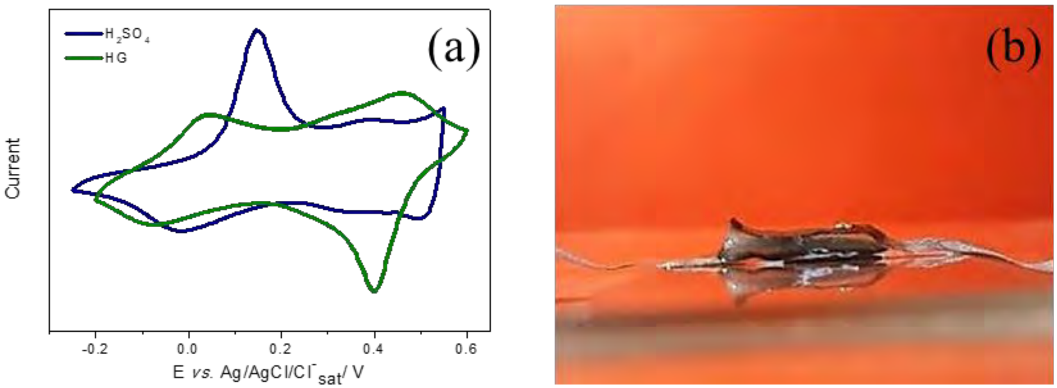
The electric power generation industry increasingly seeks to replace energy matrices based on fossil fuels with more sustainable sources. The need to develop high performance devices, capable of storing the electricity generated by these alternative sources, arises in this context. An example of devices that can perform this function are supercapacitors, which combine the high energy density of batteries with the high power density of conventional capacitors[1]. Supercapacitors have attracted the attention of researchers mainly for their versatility, once their architecture can be diversified in distinct ways, which allows their use in different applications. An application that is growing in the energy storage field is flexible and wearable electronic devices. For the development of a supercapacitor, it is necessary to have an electrode and an electrolyte. The literature is rich in studies on materials and morphologies for electrodes, however there are few studies on electrolytes, mostly on those capable of acting as electrolyte for solid devices[2]. Thus, it is interesting to develop a material that can act as an electrolyte and also present adequate viscosity, allowing its use in solid and flexible devices. In this work, a hydrogel-type electrolyte was developed from sodium alginate, a natural polysaccharide with low toxicity and low environmental impact[3]. The hydrogels were prepared from different proportions of sodium alginate, nitric acid and calcium chloride, and were characterized by cyclic voltammetry. Later, they were applied to the assembly of a supercapacitor device that combined the gel electrolyte with electrodes modified by polyaniline. The device was subjected to galvanostatic charge and discharge tests, for the evaluation of the device's specific capacitance. It was possible to establish proportions between the aforementioned reagents which allowed the charge to be transported, even with the expected diffusion limitations for an electrolyte of this type. In addition, it was possible to build a supercapacitor device in the sandwich architecture. Hereafter it is expected to test this supercapacitor device in other architectures and use this electrolyte with others conducting polymers electrodes.



The ciclic voltammetry (a) of polyaniline electrodes in H_2SO_4 1 mol L^{-1} electrolyte in blue and hydrogel electrolyte in green and a picture (b) of the supercapacitor device.

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Effects of synthesis parameters on ETFE-based anion exchange membranes and ionomers properties

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To overcome several limitations of Proton Exchange Membrane Fuel Cells (PEMFCs), anion-exchange membranes (AEM) have been developed for application in anion-exchange membrane fuel cells (AEMFC)[1]. This type of fuel cell can potentially reduce CO poisoning and allow for the possibility of using non-noble metal catalysts. Recent studies demonstrated very high performance for fuel cells containing AEMs based on the radiation-grafting of vinylbenzyl chloride onto ETFE (ethylene-tetrafluoroethylene) with a subsequent functionalization using either trimethylamine (TMA) or n-methylpiperidine (MPRD)[2]. In this work, anion exchange membranes (AEMs) based on ETFE films were synthetized under different conditions. The films were irradiated by using an electron beam source at room temperature (RT) under air or N_2 atmospheres, and also over dry ice (air atmosphere). This study evaluated the effect of dose rate and dose conditions on the grafting by vinylbenzyl chloride (VBC) and subsequently amination step. The anion exchange ionomers (AEI) responsible for conducting ions in the catalyst layer in the fuel cell are also a very important component in AEMFCs. These ETFE-AEIs, in powder form, as well as the membranes, were irradiated, grafted and functionalized by TMA. The literature presents two types of synthesis for ETFE-based AEIs: in isopropanol and in aqueous media. In the first[3], the IEC of the AEI is around 1.2 mmol g^{-1}, while in the second method[2] the IEC is around 2.0 mmol g^{-1}. However, despite this difference in IEC values, the fuel cell results are essentially the same. This is due probably to the fact that the synthesis in isopropanol provides smaller powder particles (and larger surface area in the triple phase boundary) than in the case of synthesis based on aqueous media. A major disadvantage of isopropanol synthesis is that four times more VBC is needed than in water synthesis, and this reactant is extremely toxic. Thus, besides analyzing the irradiation parameters effects on AEMs, this work also investigated the ETFE-AEIs synthesis, varying the medium, duration of the reaction and the irradiated dose. The aim was to combine smaller particle sizes with high IEC, low quantities of VBC and high final power density. AEMs synthesis results revealed that higher degree of grafting (DoG), as well as higher ion exchange capacities (IEC), are obtained at higher irradiation doses. It is important to mention that water absorption capacity follows exactly the same trend. Besides that, the switch from air to N_2 atmosphere during the irradiation process allowed higher DoGs for the same doses. For example, a membrane irradiated with 40 kGy under air normally reaches 60% of DoG after 16h of reaction, while the membrane irradiated at the same dose but under N_2 presented 82% of DoG after 16h and 63% after only 4h of reaction. The membranes irradiated on the dry ice have also shown an improvement on the DoG compared to the traditional ones irradiated at RT. At 100 kGy dose, membranes prepared over dry ice have presented 142% of DoG while membrane obtained under air results in approximately 90% of DoG. This unprecedented improvement in the way of irradiating ETFE films will allow the synthesis of membranes with the same ion exchange capacity and conductivities with lower dose rates, resulting in mechanically more stable membranes. H_2/O_2 single fuel cells tests with improved AEM and AEI showed a power density of the order of 1.13 W cm^{-2} (Fig. 1), which corresponds to a similar performance to the corresponding state-of-the-art PEMFCs obtained under similar conditions.

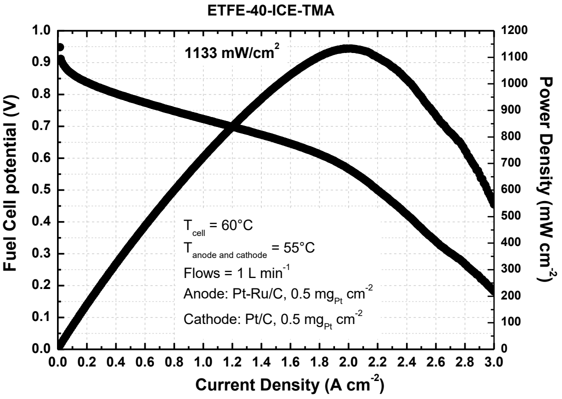

Figure 1. H_2/O_2 Fuel cells test with ETFE-AEM irradiated over dry ice.

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High detection resolution of gas and liquid products using capillary inlet DEMS setup for the CO2 reduction reaction

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Rapid analytical assessment on the electrochemical CO_2 reduction reaction (CO2RR) is fundamental for the understanding of reaction mechanism and intermediates. A special attention is given to the complexity of multiple gas and liquid products evolving during CO2RR. The current analytical techniques are limited in terms of spatially resolved product sampling, which hinders the detection of product intermediates as well as the identification of reaction processes.

In the current work, we present the assessment of products using a liquid electrochemical cell coupled through a liquid loop interface with a high-resolution mass spectrometer (DEMS technique).

Up to now, DEMS measurement are done with the specific cell design that restricts the ideal reactions conditions. Moreover, there are only few reports on kinetics onset potentials during CO2RR for Cu metal with ethylene around $-0.74\ V_{RHE}$ and methane around $-0.9\ V_{RHE}$ and a lack of analytical identification of intermediate products.

The goals of this work are to discuss the merits of combining mass spectrometer analysis with optimized electrochemistry operating conditions, to describe the methodology for direct cell DEMS measurement and thus to stimulate further development on CO2RR. Also, we will present, for the first time with DEMS, C3 oxygenates (propionaldehyde and propanol) evolution accompanied with C3 hydrocarbons, such as propane (m/z = 39,41,42), which are essential for the synthesis of cyclic and economic fuel production. In this work, we examine the products of CO2RR on copper metal catalysts and compare them for different pre-treatment conditions. For further validation of the catalyst activity assessment, we present our methodology using isotope-labeling.

The capillary inlet DEMS setup is a patented technology that will soon be commercially available at LiquidLoop, a TU Berlin Spinoff.

A Statistical Design Approach for Impedance Spectroscopy of Li-ion Battery

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Energy storage systems face challenges regarding safety and performance since they can operate under different conditions. In this sense, multiple factors can affect the performance of Li-ion batteries. Cell potential and temperature are considered major factors among them. Robust development of energy storage devices requires a deep understanding of the relationship between the operation conditions and electrochemical features. The influences of cell potential and temperature on battery parameters of commercially available $LiNiMnCoO_2$/graphite coin cells were statistically investigated and discussed by using electrochemical impedance spectroscopy combined with the Taguchi method. The experimental design provides a combination of measurements that enables fast and reliable results and detailed analyses. The experiments based on the experimental design minimize the adverse and unavoidable effects that can be defined as noises in the design terminology and increases confidence level for the results.

The Taguchi design of experiment was applied to interpret the influence of factors on the regressed elements of the developed equivalent circuit model. The synergistic effects of the battery potential and temperature on the response variables were monitored based on the statistical analysis. The factor dependency of the fitting parameters obtained from impedance response of the battery is presented in detail by a variance analysis as well as the response table.

The results showed that the sustainable Li-ion battery can be optimized in terms of battery dynamics by selecting the optimum temperature and potential obtained in this study. Temperature was determined to more significant factor compared to cell potential, suggesting that this factor should be selected carefully when the battery dynamics is desired to be optimized. This approach is suggested to be applied for different types chemistry and geometry of batteries. The results of the Taguchi design method combined with the electrochemical impedance spectroscopy would pave an effective way for the researchers improving the battery management systems in real applications.

Lithium–matrix Composite Anode Protected by a Solid Electrolyte Layer for Stable Lithium Metal Batteries

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Lithium (Li) metal with an ultrahigh specific theoretical capacity and the lowest reduction potential is strongly considered a promising anode for high-energy-density batteries. However, uncontrolled lithium dendrites and infinite volume change during repeated plating/striping cycles hinder its practical applications immensely. Herein, a house-like Li anode (housed Li) was designed to circumvent the above issues (Figure 1)[1]. The house matrix was composed of carbon fiber matrix and affords a stable structure to relieve the volume change. An artificial solid electrolyte layer was formed on composite Li metal, just like the roof of a house, which facilitates uniform Li ions diffusion and serves as a physical barrier against electrolyte corrosion. With the combination of solid electrolyte layer and matrix in the composite Li metal anode, both dendrite growth and volume expansion are remarkably inhibited. The housed Li | LiFePO4 batteries exhibited over 95% capacity retention after 500 cycles at 1.0 C in coin cell and 85% capacity retention after 80 cycles at 0.5 C in pouch cell. The rationally combination of solid electrolyte layer protection and housed framework in one Li metal anode sheds fresh insights on the design principle of a safe and long-lifespan Li metal anode for Li metal batteries.

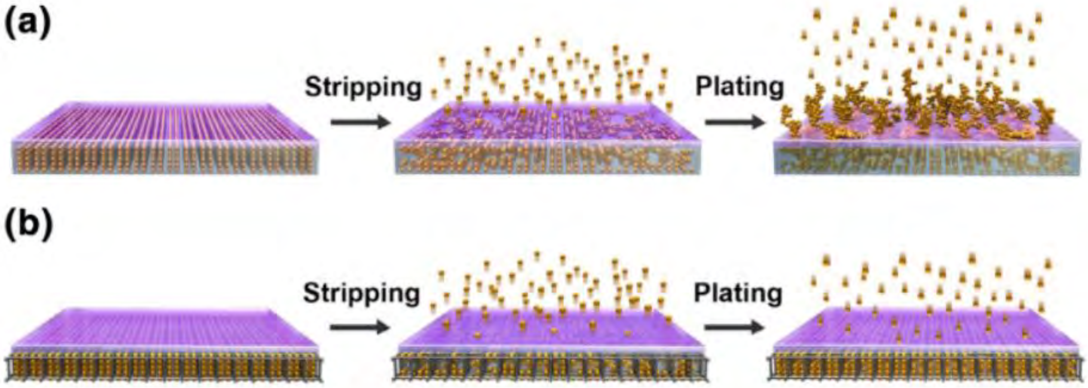

Figure 1. Schematics of morphology evolution on (a) bare Li and (b) housed Li during stripping/plating cycles.

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Effect of Process Parameters on Energy Consumption in Electrochemical Treatment of Textile Dyeing Wastewater Containing Reactive Violet 5 using Pt/Ir Electrodes

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The effect of process parameters was investigated on electrochemical treatment of textile dyeing wastewater containing Reactive Violet 5 (RV5) using Pt/Ir electrodes in the presence of 75%NaCl+25%Na_2CO_3 (w/w) supporting electrolyte mixture in a batch electrochemical reactor. Effect of process parameters were operated in the range of 300-1500 mg/L textile dye concentration, 4-20 g/L electrolyte concentration, 5-15 mA/cm^2 current density, and 20-60°C reaction temperature in 120 min electrolysis time. Decolorization yield was analyzed using UNICO 4802 model UV/Vis double beam spectrophotometer at 520 nm wavelength. Merck Spectroquant COD cell tests used for the COD analysis. Energy consumption for dye decolorization was obtained as much lower than COD removal due to the degradation of azo bond is the first step of the electrochemical degradation of the textile dyes. The energy consumption decreased with increasing textile dye concentration, electrolyte concentration and reaction temperature, while decreasing the current density. In the study, energy consumption values were evaluated for textile dye decolorization (t=15 min) and COD removal (t=120 min) as 3.8-23.5 kWh/kg dye decolorization and 64.7-321.1 kWh/kg COD removal, respectively.

Table 1. Effect of process parameters on energy consumption in electrochemical treatment of textile dyeing wastewater containing Reactive Violet 5 (RV5) using Pt/Ir electrodes

Parameter	**Process Conditions**	**E_D (kWh/kg dye decolorization) (t = 15 min)**	**E_{COD} (kWh/kg COD removal) (t = 120 min)**
Textile dye concentration	300-1500 mg/L (J=10 mA/cm^2, T=40°C, electrolyte=12 g/L)	7.4 - 22.2	100.6 - 314.7
Electrolyte concentration	4-20 g/L (J=10 mA/cm^2, T=40°C, RV5=900 mg/L)	6.4 - 20.4	111.4 - 321.1
Current density	5-15 mA/cm^2 (RV5=900 mg/L, T=40°C, electrolyte=12 g/L)	3.8 - 15.1	64.7 - 275.6
Reaction temperature	20-60°C (J=10 mA/cm^2, RV5=900 mg/L, electrolyte=12 g/L	6.8 - 10.1	134.1 - 139.6

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Interactions of plasmid DNA with new prospective antibacterial drugs: Comparison with anticancer drugs

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Anticancer drugs such as daunorubicin and doxorubicin, except for their interactions with DNA [1,2], are known to possess antibacterial properties. Moreover, some other antibacterial substances like levofloxacin [3], or nitrofurantoin [4], also interact with DNA. Question is therefore whether the electrochemical properties of new prospective antibacterial drugs might interact with DNA in a similar, or maybe in a different way than the anticancer drugs?

We have earlier studied the electrochemical properties of a new prospective anticancer drug 4-chloro-6-(1*H*-imidazo[4,5-b]phenasine-2-yl)benzene-1,3-diol (Cl-IPBD) in terms of its interactions with DNA [5, 6], using DP voltammetry to show the redox properties and ACV method to detect accumulation of the Cl-IPBD on the Glassy Carbon electrode (GCE) in terms of redox properties as well as capacitative/resistive properties. Similar strategy we are using now to study the properties of two, new prospective antibacterial drugs: 6-tert-butyl-2-(2,4-dihydroksyfenylo)-4H-tieno[3,2-d][1,3]tiazyn-4-on (TDTT), 5-(2,4-dihydroksyfenylo)-1-metylo-3-propylopirazolo[4,3-d][1,3]tiazyno-7(1H)-on (DMPT).

The difference in the conditions of the current experiments is however in the pH used. For the anticancer drugs, we have used pH 4.7, the pH often regarded as more suitable for the study of their cancer properties. This time, to obtain proper solubility of the prospective antibacterial substances, we used pH 7 to study the antibacterial drugs. For the sake of comparison, we have also tested the prospective anticancer drug Cl-IPBD at pH 7.

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Comparison of Electrochemical Degradation Kinetics of Imidacloprid and Abamectin Pesticides in Aqueous Medium using Boron-Doped Diamond Electrodes

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Electrochemical degradation of imidacloprid (IMD) and abamectin (ABA) pesticides were investigated using boron-doped diamond (BDD) electrodes in a batch electrochemical reactor. Reaction conditions were operated at 40-200 mg/L initial IMD concentration ($COD_{IMD,o}$=140-385 mg/L), 2-10 mg/L initial ABA concentration ($COD_{ABA,o}$=125-865 mg/L), 2-10 g/L supporting electrolyte (Na_2SO_4), 4-20 mA/cm^2 current density, and 20-60°C reaction temperature at 120 min reaction time. Merck Spectroquant COD cell tests used for the COD analysis. Process optimization was accomplished with response surface methodology in CCD designed experiments using Design-Expert 12 software in order to determine the effect of independent factors on COD reduction along with the experimental conditions. The optimum operating conditions under specified constraints were obtained for the highest desirability as outlined in Table 1.

Table 1. Optimum operating conditions for electrochemical degradation of imidacloprid and abamectin pesticides in aqueous medium using BDD anode

Parameter	**Imidacloprid**	**Abamectin**
Initial concentration	100 mg/L	5 mg/L
Na_2SO_4 concentration	4.4 g/L	6.4 g/L
Current density	8.6 mA/cm^2	11.8 mA/cm^2
Reaction temperature	60°C	60°C

In a batch electrochemical reactor, the overall electrochemical conversion rate of pollutants was expressed based on COD concentration. Reaction kinetics were determined by the method of initial rates, and specific reaction rate constants (k) were obtained using Arrhenius equation. The reaction kinetic parameters for electrochemical degradation of imidacloprid and abamectin pesticides in aqueous medium using boron-doped diamond anode were evaluated under response surface optimized conditions and given in Table 2. The reaction order of the electrochemical degradation of both pesticides were determined as 1. The activation energy (E_a) depends on the nature of the reaction, and fast reactions generally have small E_a values. It is known that the activation energy for a diffusion-controlled homogeneous reaction is <40 kJ/mol.

Table 2. Reaction kinetic parameters for electrochemical degradation of imidacloprid and abamectin pesticides in aqueous medium using BDD anode

Parameter	**Imidacloprid**	**Abamectin**
Reaction order (n)	1	1
Activation energy (E_a)	5.29 kJ/mol	9.28 kJ/mol
Reaction rate constant (k)	0.0105 min^{-1}	0.0100 min^{-1}
Frequency factor (k_o)	0.089 min^{-1}	0.624 min^{-1}

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Photocatalytic Activity of Electrochemically Prepared Orthorhombic MoO_3

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UV-photodegradation process can remove many organics that can not be removed from water by conventional treatments due to their chemical stability. Removal is based on oxidation via hydroxyl radical, •OH, strong oxidant produced by UV radiation. There are many attempts to catalyze the oxidation, commonly using certain oxides [1]. MoO_3 has many important applications, like in electrochromic devices and Li-ion batteries [4, 7], but it was also used as catalyst in some reactions [2, 3]; its crystal structure, activity and other properties depend on the synthesis conditions, thus several synthetic procedures are used, mostly hydrothermal [2, 3]. Electrochemical procedure was also applied due to its numerous advantages [4, 5]. In this work, MoO_3 is synthesized by galvanostatic electrodeposition, followed by thermal treatment, and used as a catalyst in UV-degradation of a dye Reactive Orange 16 (RO 16).

Electrodeposition was done in 0.05 M solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at pH 6.0 in two-electrode cell on Ti substrate (cathode) at a current density of 10 mA cm^{-2} during 90 minutes. Deposited material was peeled off, dried, and thermally treated in air at 600°C for 90 minutes. Cyclic voltammogram of Ti substrate in deposition solution was recorded in three-electrode cell using SCE as a reference electrode. The same electrode setup was used for cyclic voltammetric determination of the material band gap. The obtained material was examined by SEM, EDX, XRD and FTIR. Dye degradation was performed using the obtained material (500 mg dm^{-3}) in UV chamber at 254 nm and 1950 μW cm^{-2}.

Cyclic voltammogram contains broad cathodic peak which originates from irreversible molybdate reduction. SEM revealed micro-crystalline, mostly rod-like morphology. EDX showed the Mo:O atomic ratio % of 19.9: 80.1, which is close to the elements ration in MoO_3 with little higher O-content. XRD revealed well crystalline α-MoO_3 (orthorhombic space group 62:Pnma, parameters a =13.84, b = 3.69 0 and c = 3.96; angles $\alpha = \beta = \gamma = 90.0°$ and V = 202.33 $Å^3$). FTIR spectra contain bands between 490 and 990 cm^{-1}, typical for α-MoO_3, but there is evidence of the traces of some other MoO_3 phase, most likely h-MoO_3 [6]. The calculated band gap is 3.23 eV.

RO 16 is stable to UV radiation under the applied conditions, and it is not adsorbed by synthesized MoO_3. When exposed to UV radiation in the presence of MoO_3 catalyst, a series of RO 16 solutions ranging from 10 to 50 mg dm^{-3} was completely decolorized. Reaction takes place via •OH radicals, generated at the catalyst surface excitated UV radiation. Decolorization time increased with the increase of initial dye concentration, being about 120 minutes for the highest one. Decolorization reactions follow the pseudo-first order kinetics. Catalyst activity was 95% of its initial after 5 consecutive uses.

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One Step Electrochemical Synthesis, Characterization and Plasma Catalytic Activity of Molybdenum Zinc Oxide

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Zinc molybdates have some important applications, like supercapacitor, electronic, optical devices technology and catalysis, so several synthesis procedures have been developed, including coprecipitation, various types of hydrothermal procedures or electrochemistry – assisted laser ablation, which affects their chemical composition, crystal structure and activity [1-5]. Advanced oxidation processes, including plasma, are developed in order to degrade organic compounds which are difficult to remove by conventional procedures. Organics are successfully degraded by plasma, however, there are recent attempts to enhance this process by application of catalysts [6]. In this paper, molybdenum zinc oxide was synthesized by electrochemical procedure, and applied as a catalyst in plasma degradation of a dye reactive Orange 4 for the first time, to the best of our knowledge.

Synthesis was done in two-compartment electrochemical cell by electrodeposition at Ti cathode in the solution containing 0.01 M $(NH_4)_6Mo_7O_{24}$ and 0.1M $ZnSO_4$ at constant current density of 10mA cm^{-1} during 120 minutes. Cyclic voltammetry was performed in the same solution in three compartment cell using SCE as reference electrode. Material was peeled off the cathode and characterized by SEM. EDX and XRD. Plasma dye degradation was performed by the self-made atmospheric pressure non-thermal plasma open reactor system, based on positive pulsating corona electrical discharge. The multipoint anode was placed above the liquid surface, which acted as a cathode. The corona discharge was created in the gas phase between them. All experiments were done at 40 kHz and current density of 9.15 $\mu A/cm^2$ [7]. Catalyst concentration was 50 mg dm^{-3}.Cyclic voltammogram showed broad cathodic peak which originates from co-deposition of Zn (II) and molybdate ions. SEM analysis showed flaky morphology, with particles of undefined shapes and size varying from 1 to more than 20 µm. EDX showed the presence of Zn, Mo and O with non- uniform distribution and average atomic ratio: 16.77: 8.91:74.32%, respectively, which close their ratio in $Zn_5Mo_2O_{11}\cdot5H_2O$. XRD revealed that the synthesized material is composed of mostly rhombohedral $Zn_5Mo_2O_{11}\cdot5H_2O$, which was obtained at the cathode by co-deposition of Zn (II) species and molybdate. Some minor presence of metallic Zn, as well as some amorphous phase, most likely amorphous $Zn_5Mo_2O_{11}\cdot5H_2O$ was also detected. Dye was completely degraded by plasma treatment. Total decolorization time was lower by about 50% in the presence of catalyst in the dye initial concentration range from 5 to 40 mg dm^{-3}. Decolorization proceeds via hydroxyl radical, •OH, which is generated by decomposition of plasma-generated H_2O_2 [7].The catalyst enhances generation of •OH from H_2O_2. Degradation reactions follow the pseudo-first order kinetics. After five consecutive uses, the catalyst kept about 94% of its initial activity.

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Structural stability of K and Nb co-doping $Li_{1.167}Mn_{0.583}Ni_{0.25}O_2$ cathode material on enhanced rate and cycling performance

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The $Li_{1.167-x}K_xMn_{0.583-y}Ni_{0.25-y}Nb_{2y}O_2$ ($x = 0$, 0.05 and $2y = 0$, 0.01) samples are successfully prepared through ball mill and high-temperature treatment. The impact of K^+ and/or Nb^{5+} doping on the crystal structure, particle morphology and electrochemical properties of samples are investigated. The XRD patterns demonstrate that K^+ and/or Nb^{5+} doping does not significantly change the structure of $Li_{1.167}Mn_{0.583}Ni_{0.25}O_2$. Tiny changes in the lattice parameters of all samples indicate that K^+ and/or Nb^{5+} are successfully doped into the sample. The K^+ doping can expand the Li^+ diffusion channel and inhibit the transition of the layered structure to the spinel structure, and thus improve the cycleability and rate performance. The Nb^{5+} doping significantly improve the discharge specific capacity of the materials, but the single Nb^{5+} doping is not conducive to the cycling stability of the material. At 2C rate in a half cell, the bare LMN sample delivers capacity of 123.9 and 32.1 mAh g^{-1} at the 1st and 300th cycle, but the K^+ and/or Nb^{5+} doping significant the capacities, 141.9 and 110.2 mAh g^{-1} for LMN-K, 161.1 and 110.1 mAh g^{-1} for LMN-Nb, 162.5 and 140.6 mAh g^{-1} for LMN-K/Nb. In the full cell, the LMN-K/Nb sample also delivers the highest discharge capacities than the bare LMN and the single elemental doping samples. In addition, the XRD, SEM and XPS analysis of the positive and negative electrodes taken out from the full cell after cycling show that the crystal structure is effectively stabilized by the K^+ and Nb^{5+} co-doping, and the side reactions of the electrode and electrolyte are suppressed during the long cycle. These results demonstrated that the K^+ and Nb^{5+} co-doping are feasible strategies to enhance the performance of Li-rich layered cathode materials.

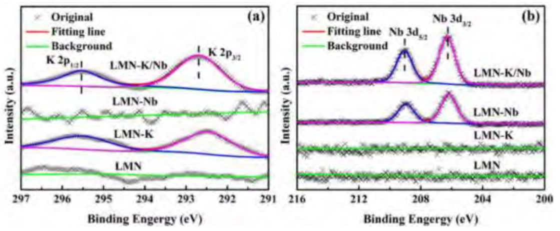

Fig. 1 XPS spectra K 2p (a) and Nb 3d (b) observed in the LMN, LMN-K, LMN-Nb and LMN-K/Nb samples.

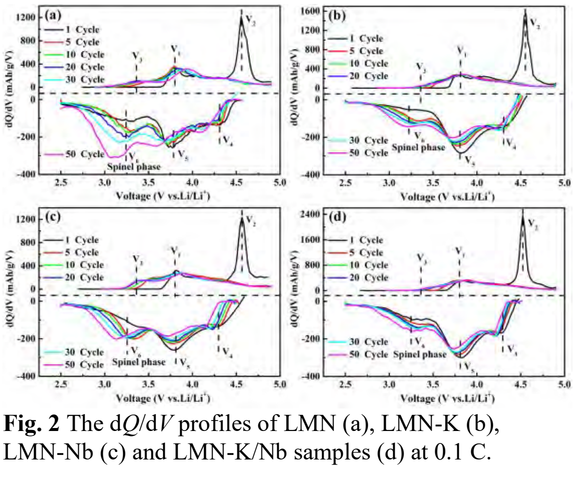

Fig. 2 The dQ/dV profiles of LMN (a), LMN-K (b), LMN-Nb (c) and LMN-K/Nb samples (d) at 0.1 C.

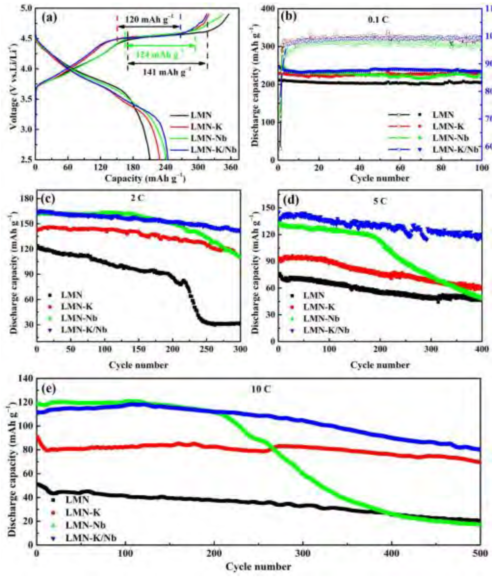

Fig. 3 The 1st charge/discharge curves (a), the cycling performances of samples at 0.1 C (b), 2 C (c), 5 C (d) and 10 C (e) rates.

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1-Hydroxyethylidene-1,1-diphosphonic acid as a corrosion inhibitor of AISI 304 stainless steel

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The novelty of this work is the analysis in a medium containing sulfide ion due to the generation of this ion in petroleum industries, in the refining stage (the sulfide ion is also present on the produced water)[1]. The performance of 1-hydroxyethylidene-1,1-diphosphonic acid inhibitor (HEDP) was investigated by potentiodynamic polarization, electrochemical impedance spectroscopy, and weight loss measurements in a dissolution of AISI 304 stainless steel immersed in a solution containing chloride and sulfide ions. The protection of the stainless was increased with the addition of divalent cations (Ca^{2+}, Zn^{2+}, and Mg^{2+}). Potentiodynamic polarization studies have shown that the inhibitor alone has anodic protection, but the addition of Ca^{2+} (10 mg L^{-1}) favors the cathodic protection, and the addition of Zn^{2+} (20 mg L^{-1}) and Mg^{2+} (10 mg L-1) mixed-type is observed. Electrochemical impedance spectroscopy was performed at three distinct potentials: -0.3 [V vs. SCE], Ecorr [V vs. SCE], and 0.1 [V vs. SCE] (see **Fig. 1**). This revealed that calcium is responsible for favoring the formation of the film and the other elements (zinc and magnesium) favor the stabilization of the protective film. Scanning electron microscopy analysis revealed that the addition of cations provided the adsorption of HEDP on the metal surface. Weight loss results showed that the presence of zinc in a solution containing HEDP favored greater inhibitor efficiency (Zn^{2+} $\eta m = 85.2\%$ and for Mg^{2+} $\eta m = 70.4\%$) [2].

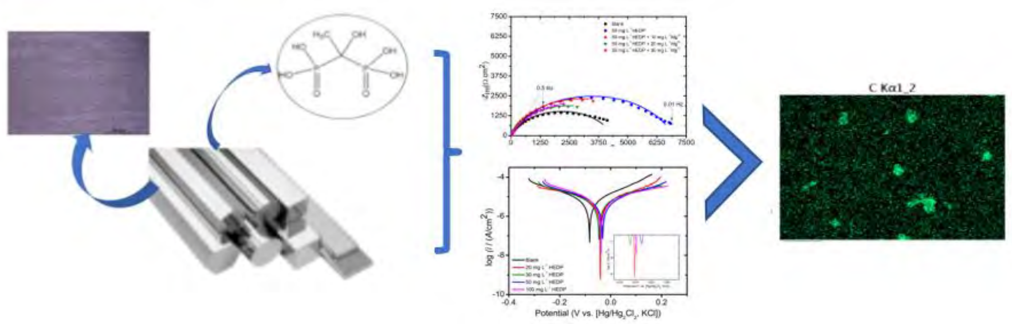

Figure 1. SEM image, EDS analysis, EIS data, and potentiodynamic polarization studies.

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Selective electroextraction of copper from aqueous leaching solutions obtained during the recycling of waste printed circuit boards using the KBr + HBr system

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The rapid development of technology and the short life of electrical and electronic equipment has resulted in the production of a large amount of waste electrical and electronic equipment (WEEE), with a production rate of two to three times higher than other urban waste [1]. The recycling process of WEEE also plays a vital role in the management of the cumulative waste from the electronics industry [2]. For all the electronic devices, the printed circuit boards are the most valuable items [3]. Their recycling can be fulfilled by using electrochemical processes which have high environmental compatibility, high energy efficiency and can be performed with minimal involvement of auxiliary materials. As a result, the recovery of metals from waste printed circuit boards (WPCB) by using electrochemical methods can reduce the reagent consumption and allows to recuperate the valuable metals without or with less loss [4].

For the selective electroextraction of copper from the leaching solutions obtained during the recycling of WPCB, in this work, cyclic voltammetry (**CV**) and selective electrodeposition of Cu in galvanostatic mode were performed. The cathodic support material was stainless steel 316.

For the beginning, measurements were performed on synthetic electrolyte solutions (**SES**) similar to the real samples (**RS**). **SES** contain KBr + HBr as supporting electrolyte background and different concentrations of $CuBr_2$ and / or $SnBr_2$ and $PbBr_2$, respectively. **CV** tests demonstrated the possibility of selective electroextraction of Cu if the electrode polarisation is more positive than the electrodeposition potential of Sn and Pb.

Selective electroextraction of copper from **RS** occurs if the Cu concentration in solution at least as 12 g/L is maintained. Selective electrodeposition of Cu is possible in a wide range of current densities, between 200 and 600 A/m^2. Under these conditions, the purity of Cu obtained deposits can exceed 99.6%.

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Study of electrodeposition parameters on the synthesis and photovoltaic response of kesterite solar cells

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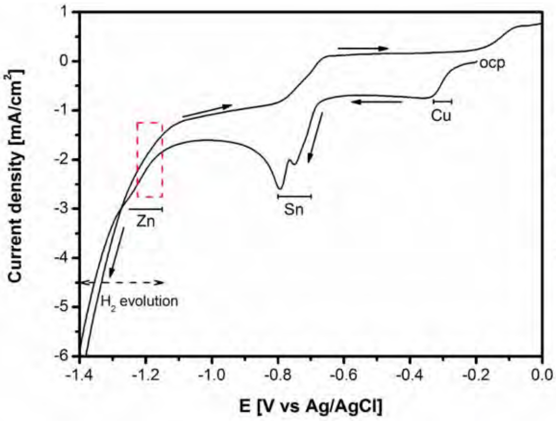
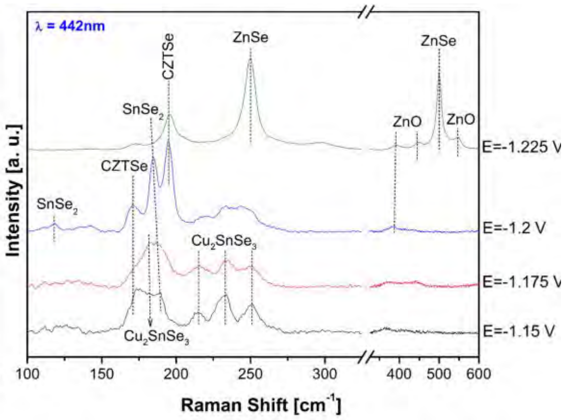
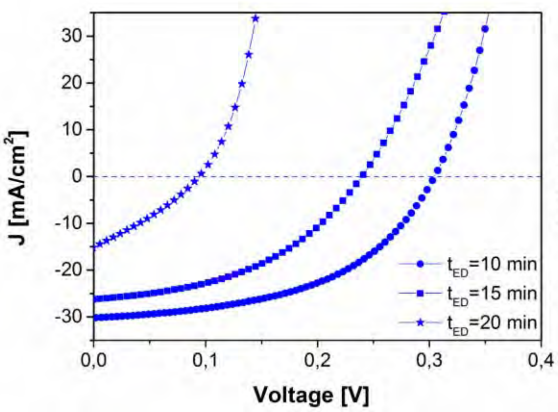
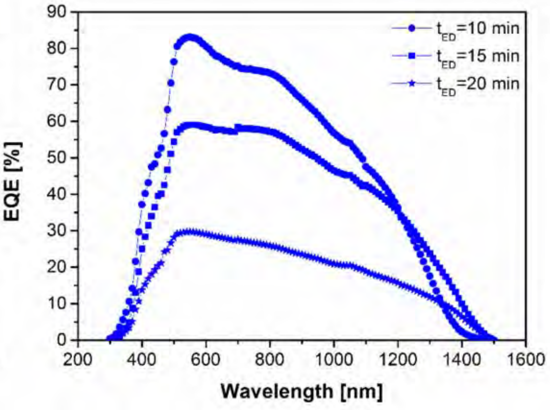
Electrodeposition is one of the most attractive techniques for the synthesis of thin films chalcogenides for photovoltaic applications, in particular for earth abundant kesterite. In this work, the influence of core parameters of this technique, such as the applied potential and deposition time, on the chemical composition of co-deposited Cu-Zn-Sn precursors is studied. Indeed, how the precursor composition affects the final composition of $Cu_2ZnSnSe_4$ after reactive annealing in Se atmosphere is also investigated, not only at the film level but also in solar cell devices. X-ray based techniques (XRF and XRD) reveal that the chemical and phase composition of electrodeposited precursors is highly sensitive to small modifications (25 mV) of the applied potential during electrodeposition. Only when the applied potential is -1.2 V (vs. Ag /AgCl) the precursor composition matches to what is required for operating devices. Multi-wavelength Raman spectroscopy of selenized precursors confirms that lower potential than -1.2 V favor the formation of Sn-rich secondary and ternary compounds after selenization, while a higher overpotential led to the formation of ZnSe in the film. On the other hand, the use of longer deposition times enhance the incorporation of zinc in the film, modifies the morphology of the precursor and promotes the formation ZnSe after selenization. Photovoltaic devices were only obtained at an electrodeposition potential of -1.2 V, and reaching a maximum efficiency close to 5% for a 10 minute electrodeposited CZT precursor.









Ternary PtCuSn Catalyst for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cells

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In fuel cells, Platinum (Pt) and its alloys have been widely used as the best electro-catalysts for the oxygen reduction reaction (ORR) owing to its intrinsic catalytic activity and stability, but its high price and scarcity limit among many major technical barriers of proton exchange membrane fuel cells (PEMFCs) still needs to be overcome in the development of electrochemical catalysts for widespread commercialization of PEMFCs [1]. In response to these issues, many researchers have been exploring novel catalyst with superior ORR activity that can effectively lessen the dependence on noble metal Pt in order to reduce the cost of fuel cells [2].

In this study, Platinum–Copper-Tin (PtCuSn) catalysts supported on carbon (XC-72R, cabot) were investigated as a cathode catalyst for oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs). The PtCuSn catalyst was synthesized via a modified polyol process in teflon-sealed reactor by microwave-heating. From X-ray diffraction and transmission electron microscopic analysis, the PtCuSn catalyst exhibits a face-centered cubic structure, similar to platinum (Pt), which is attributed to form a good solid solution of Cu atoms and Sn atoms in the Pt lattice. The PtCuSn nanoparticles with average diameter of 3.5 nm were uniformly distributed on the carbon support. The electrochemical surface area (ECSA) and ORR activity of PtCu, PtSn and PtCuSn catalysts were measured using a rotating disk electrode technique with cyclic voltammetry and the linear sweep method. The PtCuSn catalysts showed the highest performances for ECSA and ORR, which might be attributed both to formation of small nanoparticle by tin atom and to change in lattice constant of Pt by copper atom. Furthermore, The PEMFCs single cell performance employing PtCuSn catalyst exhibited an enhanced cell performance compared to a single cell using the PtCu and PtSn catalysts. This result indicates the importance of electric and geometric control of Pt alloy nanoparticles that can improve the catalytic activity. This synergistic combination of copper and Tin with Pt could provide the direction of development of Pt catalyst for fuel cell system.

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Discharge Morphology and Mechanism of Magnesium-air batteries

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Abstract:

Metal-air batteries have attracted much attentions due to their high capacity and low cost. Magnesium-air battery is one type of them with high theoretical voltage (3.1 V) and theoretical energy density (6.8 $kW\cdot h\cdot kg^{-1}$). However, magnesium (Mg) metal anode shows low anodic efficiency due to its high self-corrosion rate and discharge product accumulation on the surface. Much effort has been attempted to enhance Mg-air battery performance, but rare research has focused on the discharge mechanism of pure Mg anode in Mg-air battery. In this work, morphology of Mg anode before and after remove discharge product have been studied. Pure Mg was discharged at different current densities range from 50 $\mu A\cdot cm^{-2}$ to 5 $mA\cdot cm^{-2}$. A large amount of lamellar structure formed on Mg anode surface at low current densities, while anode surface is more uniform with pitting morphology at high current densities. Furthermore, discharge morphology of Mg metal anode shows schistose with preferred orientation. Grain boundary plays a critical role in preventing Mg self-corrosion diffusion.

Keywords: Mg-air battery, Discharge mechanism, Morphology characterization, Metal-air battery

Li-S batteries: improving polysulfide retention by cathode coating with a nanostructured carbon

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High power high-density lithium rechargeable batteries are necessary to meet the energy demand of electric vehicles and high-power stationary grids. Li-S batteries represent a potential solution to obtain high-performance electrochemical energy storage devices. This is so because of their high theoretical specific capacity 1672 mAh g^{-1} and high energy density 2600 Wh kg^{-1}.[1] However, there are many difficulties to be solved before a practical application. Sulfur has high electronic resistivity (10^{24} Ωcm)[2], and the reactions with lithium lead to an increase in volume (80%) that may result in the rupture of contact with the current collector[3]. Another important issue is the formation of long-chain polysulfides (Li_2S_n, $n \geq 4$) during sulfur lithiation. Polysulfides are soluble in the commonly used ether-based electrolytes and therefore can migrate to the anode where they undergo further reduction, which ultimately leads to the passivation of the lithium anode.[4] This process is known as the shuttle effect, which also causes the loss of active material by conversion to non-reversible structures during cycling.

In this work we use a combination of carbon structures on the cathodic side of the cell to achieve electronic and ionic conductivity, and, at the same time, the mitigation of the shuttle effect. Thus, a conductive matrix of activated carbon was just mixed with sulfur to contain the volume-change during the charge and discharge processes and to increase the conductivity of the electrode. Also, to retain the polysulfides in the cathode and prevent their migration to the anodic part of the cell a nanostructured carbon (NC), obtained from natural raw clay, was used to directly coat the sulfur cathode. XPS measurements were made on both NC-coated and uncoated cathodes, the S2*p* spectrum showed that the sulfur in the cathode interacts with the NC promoting the formation of $COSO^{2-}/SO_3^{2-}$ species before cycling. These species can help to immobilize sulfur atoms and therefore serve as mediators to retain and confine polysulfides in the cathode. Electrochemical studies of cyclability, rate capability, cyclic voltammetry, and electrochemical impedance studies (EIS) were carried out for both the pristine and NC coated cathodes. The cyclability study showed that the NC-coated cathode had excellent stability with more than 200 cycles, capacities of 75% relative to the theoretical capacity of sulfur, and coulombic efficiencies of 99.7%. The C-rate proved that this system could reach reversible capacities up to 950 mAh g^{-1} at rates as high as 1C. EIS and cyclic voltammetry showed that there is a significant increase in the electrical and ionic conductivity of the NC-coated cathode. In this manner, through a simple modification, the electrochemical performance of the system was substantially improved using simple and economic methodology.

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Increasing POM Loadings into POM@ZIF-67 Nanocomposites to Drastically Boost their Oxygen Evolution Reaction (OER) Activity

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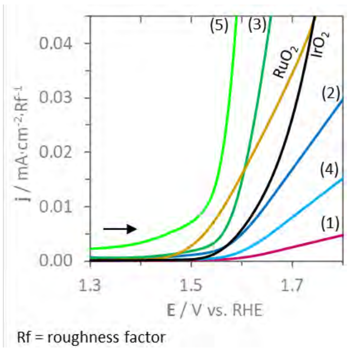
The efficient electrocatalysis of the Oxygen Evolution Reaction (OER) is a key factor regarding the real implementation of fuel cell/electrolyzer systems in industry and transport. For this reason, the development of low-cost and robust catalysts with better performances than those of the benchmark materials (RuO_2 and IrO_2) is mandatory. In this context, polyoxometalates (POMs) and metal-organic frameworks (MOFs) as well as their smart integration into electrocatalytically active nanocomposites play a protagonist role.**[1]** In our previous work,**[2]** we took advantage of the complete size complementarity between zeolitic imidazole frameworks (ZIFs) cavities and Keggin-type POM units and prepared two POM(guest)@ZIF(host) materials involving individually encapsulated SiW_9Co_3 POM units inside the ZIF cages. By using two isostructural ZIF frameworks —ZIF-8 and ZIF-67, including Zn and Co nodes, respectively— we demonstrated the necessity of the existence of Co nodes in the ZIF frameworks to generate a POM ↔ ZIF-67 bidirectional synergy leading to a significant OER activity. Now, we have extended this phenomenon to another more easily synthetized cobalt-containing POM, $SiW_{11}Co$, and successfully increased the POM loadings.**[3]** Interestingly, the resulting high POM loading nanocomposites (labelled as $SiW_{11}Co$[h]@ZIF-67 and SiW_9Co_3[h]@ZIF-67) present extremely modified frameworks far away from the canonical ZIF structures, being these drastic structural changes —along with the POM loading increments themselves— the origin of their boosted OER activities. A thorough compositional/structural characterization (via ICP-OES, XPS, ATR-IR, PXRD, N_2-adsorption, SEM, TEM and EDS analysis) revealed the coexistence of two structurally/morphologically differentiated phases in these complex electrocatalysts, both of them including homogeneously dispersed POM clusters. In addition, CV, LSV and chronoamperometric tests allowed the estimation of the ECSAs and OER activities developed by these samples in alkaline electrolyte and their long-term stability as well. These tests have shown up a remarkable OER performance of the POM@ZIF-67 nanocomposites, much higher than that exhibited by the pristine ZIF-67 (**Table 1**), and an intrinsic activity comparable —and, in some cases, even higher— to the expensive commercial RuO_2 and IrO_2 powders (**Figure 1**).

Table 1. OER activity parameters of pristine ZIF-67 and POM@ZIF-67 nanocomposites.

	OER parameter			
(ref) sample	E_{10} (V *vs. RHE*)	η_{10} (V)	$j_{1.75}$ (mA cm^{-2})	*Tafel Slope* (mV dec^{-1})
(1) ZIF-67	1.81	0.58	7.2	144.3
(2) $SiW_{11}Co$@ZIF-67	1.69	0.46	15.0	141.6
(3) $SiW_{11}Co$[h]@ZIF-67	1.66	0.43	23.0	95.3
(4) SiW_9Co_3@ZIF-67	1.70	0.47	14.2	113.6
(5) SiW_9Co_3[h]@ZIF-67	1.65	0.42	28.9	93.9

Figure 1. OER LSV curves of pristine ZIF-67, POM@ZIF-67 nanocomposites and reference materials.



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Using Ionic Liquids to Increase Selectivity and Sensitivity in Heavy Metal Ion Detection

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Electrochemical sensing of heavy metal traces, such as Pb, Cd and Hg is known to be a user-friendly, mobile point-of-care solution. High sensitivity can be obtained by electrochemical methods, such as square wave anodic stripping voltammetry (SWASV) in presence of surface modifiers (e.g. Hg or Bi), as reflected by impressive limits of detection far below WHO suggestions. Nevertheless, unsatisfying selectivity as also low stability hinders vast commercialization of electrochemical detection in this field. Liu-Liu et al. demonstrated that modifier free sensors using technical grade graphite foil can exhibit high stability and also satisfying sensitivity [1]. The current work aims to use ionic liquids (ILs) to further improve the selectivity and sensitivity based on the modifier free concept. ILs are capable of selectively extracting and preconcentrating heavy metals from aqueous solutions due to their high solubilities in ILs, which provides the basis for this study. As a suitable IL protonated betaine bis(trifluoromethane)sulfonimide [HBet][NTf_2] was chosen as it combines two crucial properties: 1) It extracts metal ions from aqueous phase with different distribution coefficients, enabling discriminating preconcentration [2] and 2) it is reported for the direct electrochemical detection of metal oxides in the sub-ppb range [3]. Furthermore, for the first step of extraction this IL allows for facile and intensive mixing as also phase separation, as above the upper critical solution temperature of 55 °C a homogeneous mixture occurs and below phase separation is induced. As a conceptual study the extraction of Pb-ions from aqueous phase, temperature induced phase separation and subsequent ion detection via SWASV was investigated using only technical grade graphite foil as working and counter electrodes (Fig. 1 A). A reproducible extraction and detection of Pb^{2+} for concentrations of 2 ppm in the aqueous phase can be realized and SWASV-peaks of several 100 µA resulted (Fig. 1 B). Future work can build on this concept, which is especially promising for improving selectivity.

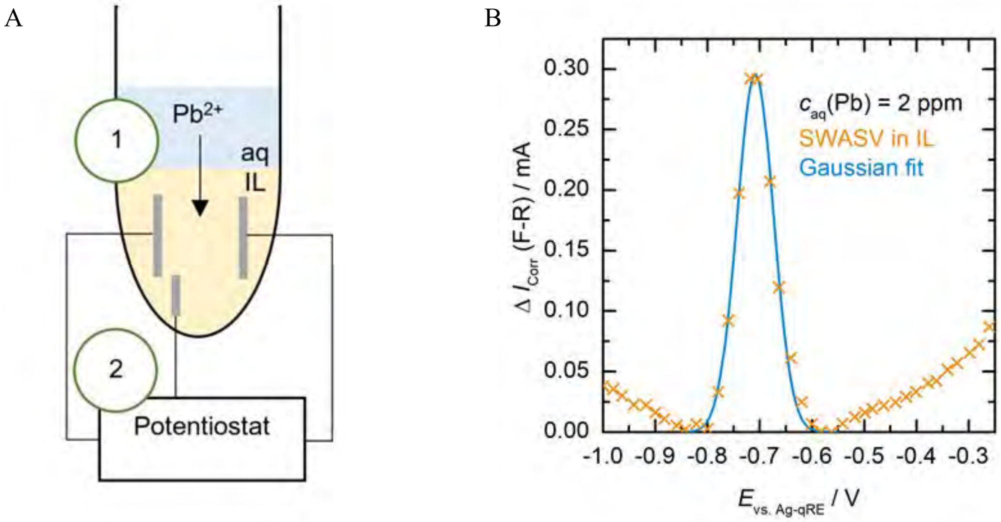

Fig. 1 A: schematic procedure of the Pb^{2+} extraction (step 1) from the aqueous to the IL phase ($V_{IL}/V_{aq}=1$) via single-phase-generation and the electrochemical detection (step 2) by SWASV. B: SWASV response signal for a starting concentration of 2 ppm Pb in the aqueous phase (parameter: deposition: 10 min @ -1 V *vs.* Ag-qRE, stripping: f=100 Hz, E_P=100 mV, E_S=20 mV).

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The design of a new electrochemical cell for studying highly active metalloenzymes

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Protein Film Electrochemistry is a technique consisting in immobilizing enzymes on a rotating disc electrode in a configuration where the electron transfer is direct, and the enzymatic activity is monitored as an electrical current [Figure 1]. This technique has proved extremely useful to study various aspects of the activity of metalloenzymes [1]. Generally, the consumption of the substrate at the surface of the electrode is compensated by a flow of a fresh buffer imposed by the rotation of the electrode. However, this was not the case for CO dehydrogenase (CODH), which is an enzyme that catalyzes the reversible reduction of CO_2 into CO following this equation: $CO_2 + 2e^- + 2H^+ \leftrightarrows CO + H_2O$

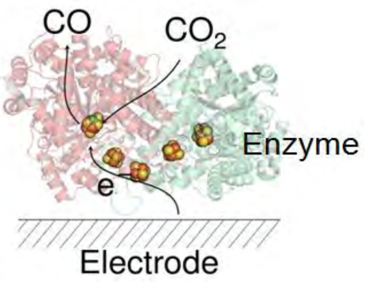

Figure 1. schematic representation of protein film electrochemistry

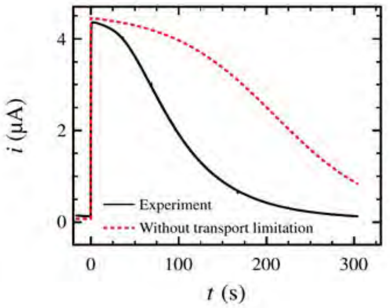

Figure 2. experiment in which the CODH is exposed to a transient injection of CO

This enzyme is so fast that the catalysis is mostly limited by the transport of the substrate (CO) towards the electrode, and not by the catalyzed chemical reaction, even at a high rotation rate. This limitation hides information about the catalysis in the electrochemical response [2] [Figure 2]. As this problem couldn't be overcame by the rotating disc electrode, we chose to design a completely different type of electrochemical cells (based on jet flow cell) in which the buffer is pumped towards a static electrode [3].

We screened different jet flow cell geometries by means of numerical simulation. Then, we selected and built one with promising transport properties (a high and homogenous mass transport coefficient, and a low shear stress at the surface of the electrode) [4]. In this work, we optimize the current design by simulation, and we further test the performance of the new setup experimentally by using simple redox couples such as Fe $(CN_6)^3$/ Fe $(CN_6)^{3-}$ or by detecting the catalytic current given by an adsorbed enzyme, the nitrite reductase which catalyzes the reduction of nitrite to ammonium. This new cell should provide enhanced transport but also a much greater flexibility for changing the concentration of the species that the enzyme is exposed to. Therefore, it will be useful for studying other metalloenzymes that do not even require high mass transport.

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Redox-Driven Deformation and Electrode Reaction of Viologen-Incorporated Polymer Hydrogel

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Stimuli-sensitive hydrogels have a wide variety of flexibility and mobility. They can be used as a material of an actuator in an assembled molecular robot. We focused on a redox driven hydrogel, because redox reaction in the gel can quickly and drastically change the properties of the gel, resulting in fast and large-scale motion of the gel. With an aim at developing redox driven hydrogel, we use redox reaction of viologen (**Figure 1a**) as the engine of fast and large amplitude deformation. We designed a hydrogel shown in **Figure 1b**. Viologens were covalently attached via amide linkage to poly-peptide, α-poly-*L*-lysine (PLL). Then, glutaraldehyde was used for cross-linking of free ε-amine groups to give a hydrogel, PLLV gel. The hydrogel with a 25% viologen pendant rate contracted 93%-volume within 100 s upon reduction of viologens by dithionite, whereas it exhibited slow re-expansion upon reoxidation by dissolved O_2 [1]. One-electron reduction of a viologen (V^{2+}) to radical cation $V^{\bullet+}$ induces the stacking of $V^{\bullet+}$ units and desolvation of the viologen sites. The former process draws the polymer chains to be entangled and to accelerate inter-site electron transfer, while the latter process drains water from the gel (**Figure 1c**). A decrease of positive charges on viologens results in the change of osmotic pressure to egress of water from the gel. All these changes upon reduction contributed to the contradiction of the hydrogel.

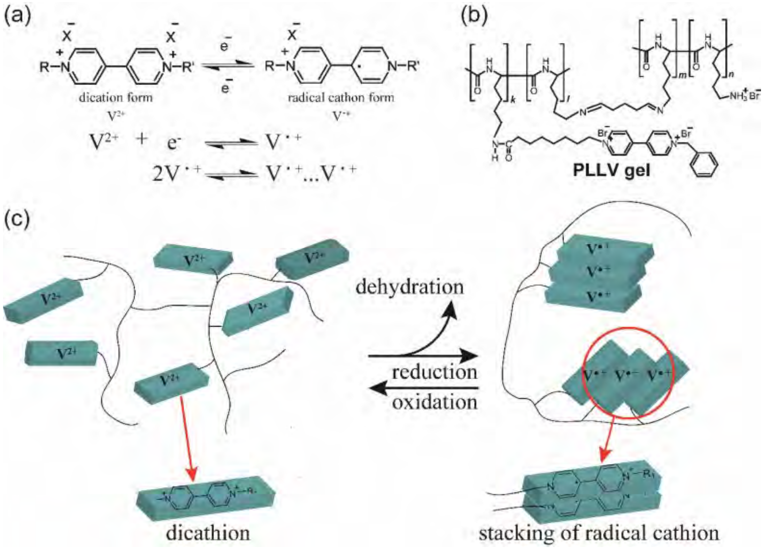

Figure 1. Chemical structure and redox process of viologen (a), chemical structure of PLLV gel (b), and mechanism of target hydrogel deformation (c).

Electrochemical and spectroelectrochemical characterization of the PLLV gel was made by sandwiching a piece of gel between a Au disk electrode and the inner wall of an optical window of the cell. We observed cyclic voltammetric response of apparent diffusion in the range of sweep rate between 2 and 200 mV s^{-1}. The feature of obtained electroreflectance spectra was of the enriched $V^{\bullet+}$ dimers.

We examined the effect of the viologen pendant rate as well as the introduction of a conductive filler and polymer electrolyte counter anion. The 25% pendant rate gel showed contraction faster and larger amplitude than the others. We added conductive fillers in the gel for accelerating electron transportation and re-expansion. The fillers included Au nanoparticle, graphene nano-platelet, and carbon nanotube. The initial contraction of the gel with fillers was faster than the gel without fillers. However, re-oxidative swelling was still slow. The contraction and re-swelling largely rely on egress and ingress of water. To boost the penetration of water and accelerate re-oxidative swelling, the anionic polymer, polystyrene sulfonate (PSS), was incorporated into the gel. The incorporation made the re-oxidative swelling faster and the swelling amount greater. PSS accelerated water ingress into the gel and made the re-oxidation swelling faster and the extent larger, while it diminished the contraction amplitude.

These results pave a new way to a hydrogel crawling on an electrode by redox control.

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TiO2/SnO2 nanocomposites for lithium-ion batteries

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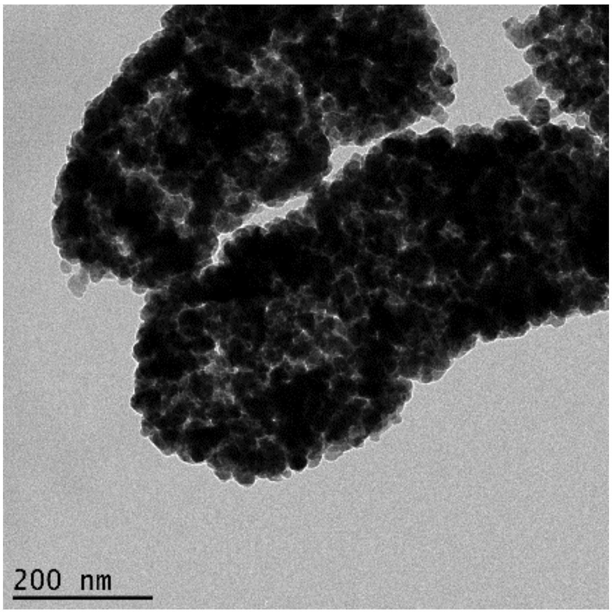
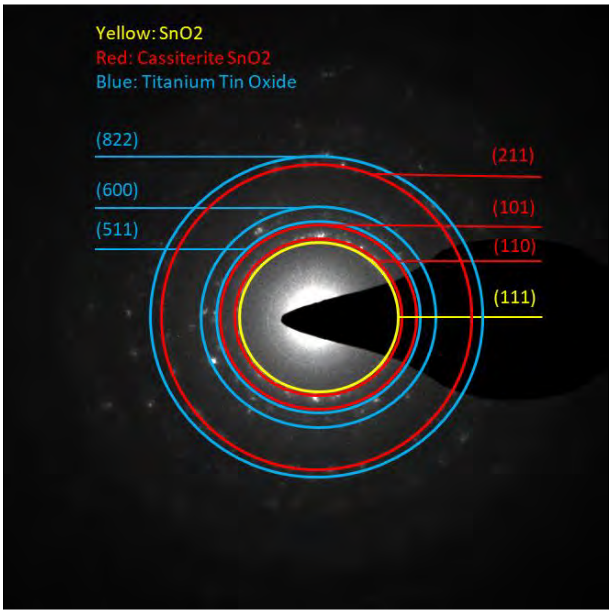
Lithium-ion batteries(LIBs) have been widely used as electrical energy storage (EES) devices for portable electronic devices, such as laptops and smart phones. LIBs are also being considering as EES system for electric vehicles and grid scale energy storage. These applications require batteries have higher energy density and lower cost. [1]. In present study, TiO2/SnO2 nanocomposites have been synthesized as anode materials for lithium ion batteries. Firstly, Tin(II) oxide hydroxide was synthesized with sol-gel method, and then coated with TiO2 by using wet chemistry method. The tin(II) oxide hydroxides are pyramid-shape nanoparticles. TiO2 coated pyramid-shape nanoparticles were heated at 600°C to form TiO2/SnO2 hollow nanocomposites(TSHNP). These nanocomposites show a unique hollow structure with particle size about 200 nm, and original pyramid structure was destroyed during the oxidation process in the heat treatment. The TiO2/SnO2 nanocomposites have been tested as an anode for lithium ion batteries in half-cell. Compared to SnO2, TSHNP shows longer cycle life with maintaining 200 mhA/g in 50 cycles, which is due to the special hollow structure[2]. In addition, TiO2 and Li2O matrix act as a mechanical support system for SnO2 volume expansion during the de/lithiation process. However, C-rate performance are not ideal because of the polarization and relatively low electron conductivity, which are the challenges of transition metal-oxides.





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Coupling Micro-Hydropower with electrolyzing, case study

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The energy used to pump and treat water for residents and industry represents between 2 and 3% of the world's energy consumption {1}. The consumption can be reduced by 25% through solutions like micro-hydropower (MHP). Pressure reducing valves (PRV) are installed in the water distribution network (WDN) to reduce the leakage losses, which is directly related to the pressure in pipe {2}. The reducing of pressure in PRVs lead to hydraulic losses into thermal losses, replace PRV with MHP system is a good solution to recover a part of those losses. On the other hand, the transport area, with a thermal motor, is one of the main issues for slowing global warming. Replace thermal motor with electrical motor supplied by fuel cells is a good solution. One of the biggest water tanks in Rennes (France) called "Les Gallets" is an interesting site to implement MHP installation, the huge site area allows to implement a electrolyze installation to supply hydrogen cars. Coupling the production of hydrogen with MHP system is a solution to get a green energy production. The scheme of the installation is presented in figure 1.

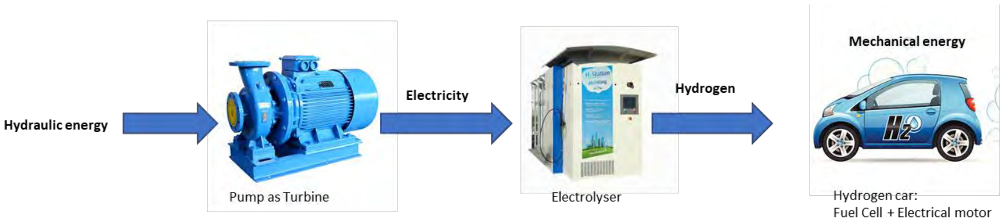

Figure 1: Installation's scheme

The site "Les Gallets" is composed of two water tanks, one is called "Les Gallets Haut", the other one is called "Les Gallets Bas". Two MHP systems can be installed, one upstream the first water tank, and one between both water tanks. Conventional turbines are not massively available on the market, hence they are expensive and lead to strong payback periods for MHP, to face this problem, the use of pumps in reverse mode (pumps as turbines) is a solution {3}. Indeed, those pumps have good efficiencies (between 50 to 85%) and can be divided by 10 times the payback period of an installation compared to conventional turbines installations. For this study, an average efficiency of 65% for Pumps as turbines installations is considered.

Flow conditions of both installations are detailed in table 1.

Site	Flow rate (l/s)	Head (m)	Load factor (h/year)	E_{lost} (MWh/year)	Producible (MWh/year)	H_2 Producible (kg H_2/year)
Gallets Haut	208	11	7366	165,7	107,705	1795
Gallets Bas	100	19	6647	137,6	89,44	1490

Table 1: Flow conditions of Gallets sites

The total electricity production in "Les Gallets" will reach about 197MWh per year. Considering that the electrolyzer absorb 60 kWh of electricity to create 1kg of Hydrogen. The electrolyzer will be able to produce about 3285kg of H_2 per year. Considering a conventional Hydrogen car, with an autonomy of 500km, and a Hydrogen's consumption of 1kg of H_2/100km, it will be possible to load the car's fuel cell 625 times per year.

Acknowledgements to Eurepean InteReg EERES4WATER and Brittany region.

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Nitrogen-rich covalent organic frameworks for high-performance sodium batteries

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Covalent organic frameworks (COFs) have attracted increasing attention as idea cathode materials duo to the designable periodic skeletons and ordered nanopores. However, the reported COFs based cathode materials are plagued by limited capacity and unsatisfying rate performance. Herein, we designed a honeycomb-like nitrogen-rich COF (TQBQ-COF) with good intrinsic electronic conductivity and studied the electrochemical performance in sodium battery. The sodium storage ability of pyrazines and carbonyls and the up-to twelve sodium-ion redox chemistry mechanism for each repetitive unit have been demonstrated by in/ex-situ Fourier transform infrared spectra and density functional theory calculations. The TQBQ-COF cathode exhibits high capacity of 452 mAh/g (0.02A/g), excellent cycling stability (96% capacity retention after 1000 cycles), and high rate performance (134.3 mAh/g at 10 A/g). A pouch-type battery (energy density of 101.1 Wh/kg) is assembled to prove practical applications of conjugated polymers in rechargeable sodium batteries. This work will promote the function-oriented design and application of COFs-based materials for high-performance sodium storage devices.

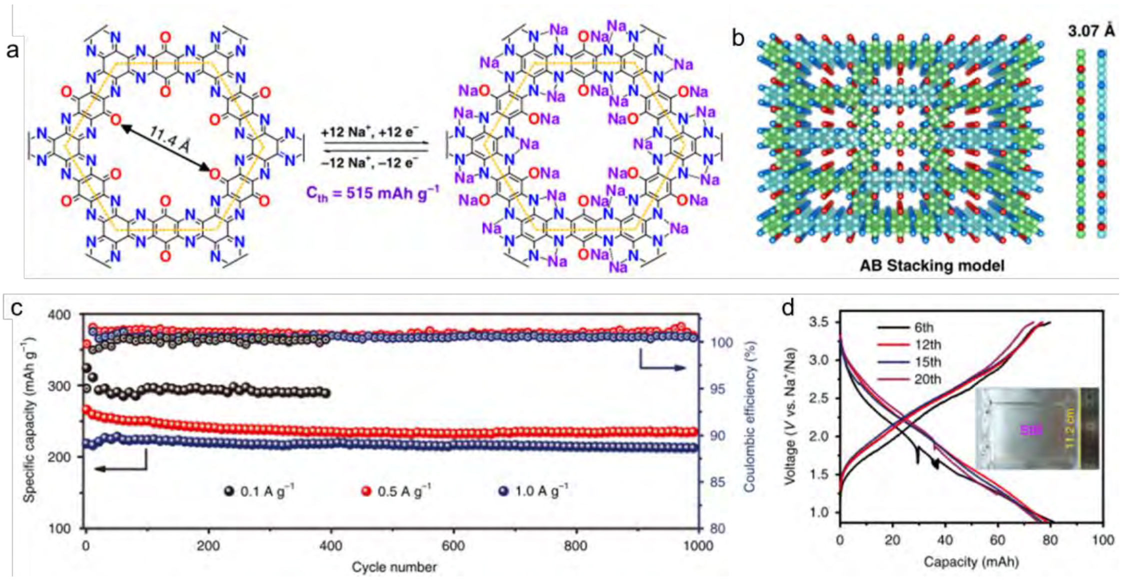

Figure 1. (a)The chemical structure and possible electrochemical redox mechanism of TQBQ-COF with a theoretical capacity of 515 mAh/g. (b) Top and side views of the schematic AB stacking model of TQBQ-COF layers with a packing distance of 3.07 Å. (c) Long cycling stability of TQBQ-COF electrodes at different current densities (0.1, 0.5, and 1.0 A g^{-1}). The capacities are all calculated based on the mass of TQBQ-COF. (d) The selected charge/discharge curves of pouch-type Na//TQBQ-COF batteries at a current of 50 mA. The capacity is calculated based on the mass of the full cell.

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Photovoltaic activity of simple photosystem I/conducting glass electrode

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We demonstrate photovoltaic activity of electrodes composed of fluorine-doped tin oxide (FTO) conducting glass and a multilayer of trimeric photosystem I (PSI) from cyanobacterium *Synechocystis sp.* PCC 6803 yielding, at open circuit potential (OCP) of + 100 mV (vs. SHE), internal quantum efficiency of (0.37 ± 0.11)% and photocurrent density of up to (0.5 ± 0.1) $\mu A/cm^2$.[1] The photocurrent measured for OCP is of cathodic nature meaning that preferentially the electrons are injected from the conducting layer of the FTO glass to the photooxidized PSI primary electron donor, $P700^+$, and further transferred from the photoreduced final electron acceptor of PSI, F_b^-, via ascorbate electrolyte to the counter electrode. This observation is consistent with preferential donor-side orientation of PSI on FTO imposed by applied electrodeposition. However, by applying high-positive bias (+ 620 mV) to the PSI-FTO electrode, exceeding redox midpoint potential of P700 (+ 450 mV), the photocurrent reverses its orientation and becomes anodic. This is explained by "switching off" the natural photoactivity of PSI particles (by the electrochemical oxidation of P700 to $P700^+$) and "switching on" the anodic photocurrent from PSI antenna Chls prone to photooxidation at high potentials. The efficient control of the P700 redox state (P700 or $P700^+$) by external bias applied to the PSI-FTO electrodes was evidenced by ultrafast transient absorption spectroscopy. The advantage of the presented system is its structural simplicity together with in situ-proven high intactness of the PSI particles.

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Magnesium and Calcium Insertion/De-insertion into the Sb Modified Au Electrode and determination of the diffusions coefficients

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Antimony has been suggested as an insertion material for a magnesium secondary battery [1, 2], because magnesium can form an intermetallic binary phase Mg_3Sb_2. The stable alloy reaction shows high magnesium storage performance and high cycling stability.

The diffusion coefficient of Mg-insertion in Sb - multi-layers has been estimated by using various electrochemical techniques. We studied the diffusion of Mg in a thin, bulk (massive) layer of Sb by using PITT, CV and potential step experiments. Such diffusion coefficients, albeit still somewhat "apparent", are much related to true diffusion coefficient in the metal or alloy. The diffusion coefficient of Mg into the Sb layers are in the range of 10^{-13}-$10^{-15}$$cm^2s^{-1}$. The D_{Mg} values was calculated by CV at about $1.28 - 1.78 \times 10^{-14}\ cm^2/s$ into a novel Bi-based anode (Bismuth oxyfluoride, BiOF) [3] and as $1.97 \times 10^{-14}\ cm^2/s$ into a CuS cathode by GITT-Method. [4]

Recently calcium stripping and plating using a $Ca(BH_4)_2$ electrolyte was reported at room temperature with a Coulombic efficiency (CE) of 95% on an Au substrate. [5] In this work the insertion/de-insertion of Ca^{2+}-ion into antimony with $Ca(BH_4)_2$/THF electrolyte was investigated. The cyclic voltammogram for Ca insertion/de-insertion into Sb-modified electrode shows a positive shift (~1 V) of the onset potential of Ca deposition compared to that at bare Au electrode. The ratio of moles of Ca to Sb agrees with the stoichiometry of Ca_2Sb alloy. The diffusion coefficient of Ca into the Sb layers are calculated to be $4.25 - 6.11 \times 10^{-15}\ cm^2/s$ cm^2s^{-1}.

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Investigation of diffusion coefficients of the hydroxide ions of various systems using a rotating electrode setup

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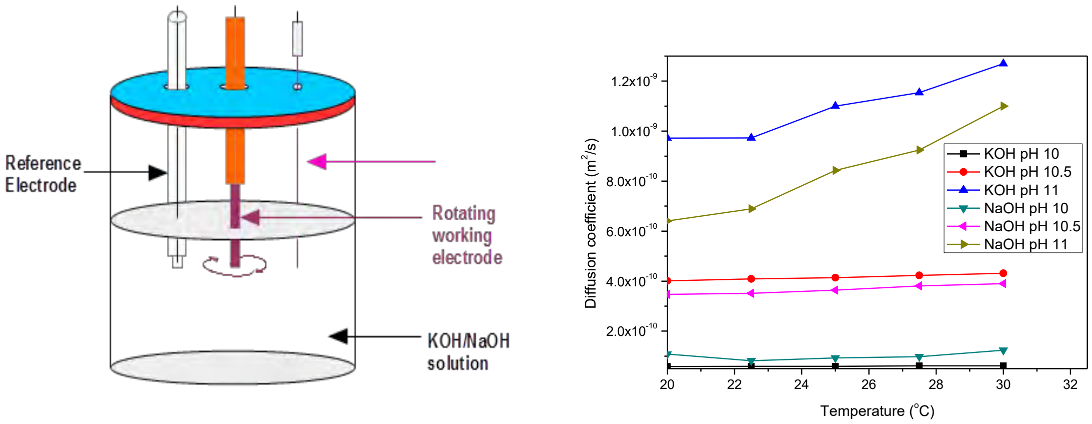
Hydrogen [1,2] is one of the most promising energy carriers for domestic and industrial energy systems. Water electrolysis is considered as the safest and non-polluting means of producing the hydrogen. Rotating disk electrode is a hydrodynamic electrode technique that utilizes convection as the mode of mass transport. In order to determine the diffusion coefficient of hydroxide ions, Levich's theory [3] can be used. This theory makes it possible to calculate the diffusion limit current of a sample placed on a rotating disc electrode.

$$J_{lim} = 0.62 nFD^{\frac{2}{3}}\Omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}C$$

With the help of the above equation value of D can be extracted. Here, the experimental set-up is a three-electrode arrangement as shown in Figure 1.A. The rotating disc electrode is placed in the centre of the beaker to avoid boundary problems and to have forced convection due to the invariant electrode by rotating it around the electrode. The counter electrode and the reference electrode are placed about two centimetres from the working electrode. NaOH and KOH solutions with different concentration are used as the electrolyte. Voltage and current data are recorded using the Nova control software and the electrochemical technique used is linear scanning voltage (LSV) voltammetry, with the potential being reset to 0 between two experiments using a second LSV. We also extracted the value of the diffusion coefficient with different temperatures as shown in Figure 1.B. It is observed that the diffusion coefficients tend to increase with temperature.



A B

Figure 1: (A) Experimental setup (B) The sensitivity of the diffusion coefficient with respect to the temperature

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Novel Experimental Approach for the Direct Assessment of Nucleation Rate Constants from Cyclic Voltammetry and Chronoamperometry Data for Phase Transforming Intercalation Electrodes

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Phase-transforming electrode materials with a wide miscibility gap have been extensively studied for both Li-ion ($LiFePO_4$, $Li_4Ti_5O_{12}$) and Na-ion ($Na_3V_2(PO_4)_3$) batteries. In particular, $LiFePO_4$ material has become a model system for the investigation of intercalation induced phase transformation mechanisms.[1,2] Most of the state-of-the-art research on the phase-separating intercalation materials focuses on the elucidation of phase transformation mechanisms as well as on the theoretical assessment of the nucleation barrier heights based on the evidence from structural investigation and microscopic single particle-level experiments.[3] In particular, recent reports have led to the establishment of a concept of competing mechanisms of phase boundary propagation, which can be bulk diffusion limited or surface reaction limited.[4] Yet, phase-field modeling usually used to rationalize the experimental findings rarely relies on the experimental values of nucleation and charge transfer activation barriers, deduced directly from the experimental data, which compromises the reliability of the obtained results.

Recently developed electroanalytical methods[5,6] provide the possibility to estimate the characteristic rates of nucleation, charge transfer and diffusion from the experimental electrochemical data. The proposed novel approaches enable direct comparison of phase transformation rates in various intercalation-based electrodes ($LiFePO_4$, V_2O_5, cation-rich Prussian blue analogues, $Na_3V_2(PO_4)_3$) as well as the elucidation of the rate-determining step nature. In this work, we show that the new phase nucleation appears to be a characteristic rate-determining step for a wide range of intercalation materials. We demonstrate that the nucleation rates (probabilities of critical nucleus formation) can be straightforwardly determined from the electrochemical experimental data. A simple experimental approach is proposed toward interpreting electrochemical cyclic voltammetry and chronoamperometry data for phase-transforming electrodes.[7,8] The new methodology provides for a facile assessment of the influence of various experimental factors (particle size, defect concentration, solvent nature, and surface coating) on the nucleation-controlled phase-transformation rates in intercalation materials. Experimental data analysis illustrates the validity of the applied approaches, which allows developing diagnostic criteria for distinguishing slow nucleation rate control from other possible rate-determining steps as well as obtaining quantitative estimates of the nucleation rate constants.

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Iron Sulfide-Carbon Nanospindles as Sulfur Host for Li-S Batteries

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Recently, a lot of efforts are devoted into lithium-sulfur battery system due to its high theoretical capacity (1675 mAh g^{-1}) and low cost, which could be a competitive candidate for energy storage in the future. However, it suffers from a poor cycling stability during charging-discharging, which is blamed to the notorious "shuttle effects" caused by lithium polysulfides (Li_2S_x, $4 \leq x \leq 8$) [1-2]. In our study, functional metal oxide/sulfide nanoparticles prepared by a colloidal route have been used as cathode host materials for lithium-sulfur batteries. Firstly, β-FeOOH nanospindles with a length of 250-300 nm and a diameter of 60 nm were successfully synthesized through the hydrolysis of $FeCl_3$ in cetyltrimethylammonium bromide (CTAB) solution in a large batch [3]. After coating with polydopamine and followed with annealing at high temperature, iron oxide/sulfide was designed to be encapsulated into hollow cabon nanospindle with formation of a york-shell structure(shown in Fig.1) to suppress the "shuttle effect". An improved performance has been obtained via the combination of physical adsorption of the hollow carbon nanospindle and chemical adsorption of iron sulfide. Moreover, it is revealed that the replacement of iron oxide with sulfide inside the hollow carbon spindle can improve the specific capacity and rate capability of the lithium-sulfur batteries.

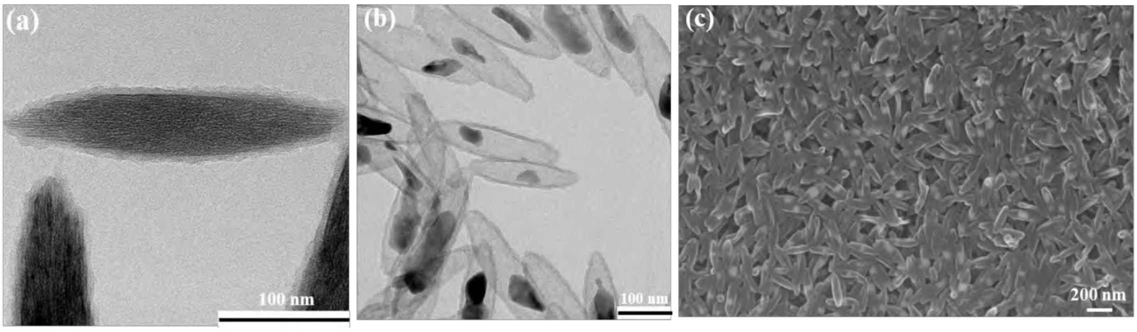

Fig. 1: TEM and SEM images of polydopamine coated FeOOH nanospindles (a), Fe_3O_4-carbon yolk-shell nanospindles (b) after etching 2 h with HCl solution (2 M) and FeS-carbon yolk-shell nanospindles (c).

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Electrochemical Readout of Molecularly Imprinted Polymers: Potentials and Challenges

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Molecularly imprinted polymers (MIPs) are one of the most frequently studied alternative recognition elements in chromatography and sensorics. They are prepared by polymerizing the target analyte (so-called template) and functional monomers (in the presence or absence of cross-linkers). Subsequent removal of the template from the polymer network results in the formation of cavities with a molecular memory, which is complementary in size, shape and functionality to the template [1].

Depending on the analyte of interest, three main approaches have been presented in literature for the electrochemical readout of MIP sensors [1]. Herein we present examples for each approach.

i) Electroactive analytes: For both low- and high-molecular weight targets, faradaic current is measured, which is based on the direct redox transformation of the analyte at the electrode. The analytical performance of MIPs for the anticancer drug tamoxifen and the enzyme hexameric tyrosine-coordinated heme protein will be demonstrated [2,3].

ii) Catalytically active analytes: In the second approach redox active products of enzymes, catalytically active MIPs or enzyme-labelled tracers can be directly measured. In this regard, MIPs for the Alzheimer´s disease biomarker butrylcholinesterase and the melanoma biomarker tyrosinase will be illustrated here [4,5].

iii) Redox-inactive analytes: The most frequently studied method relies on the modulation of diffusional permeability of the polymer MIP-layer by target binding of a redox marker. MIPs for the peptide drug daptomycin and the anticancer drug tamoxifen will be presented [3,6].

In this presentation the potential and challenges of electrochemical readout of MIP sensors will be summarized: Electrochemical methods are straightforward for the preparation of MIPs and analyte determination. However, up to now there has been no commercial example yet.

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Electroosmotic pump for implantable drug delivery system

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An implantable infusion pump is surgically implanted in the abdomen to deliver a drug to a target area through a catheter. It is beneficial for severe chronic and cancer pain patients. For the acute pain, morphine delivers directly to the intrathecal space, where the main neuro signals pass by. The amount of 1/100th or 1/300th amount of the drug has the same efficacy of the delivery through intravenous or oral. The programmed intrathecal delivery significantly increases the patient's quality of life by reducing the side effects of the medication since the drug does not circulate through the whole body. The electroosmotic pump (EOP) consists of two electrodes separated by a porous membrane, having no magnetic component, and ideal for the implantable device. We could demonstrate that the device is MRI compatible even during the run. The sub μL/min flow rate, low-power consumption, and long-term stability confirm the pump is suitable for the implantable drug delivery.

Electrooxidation of Hydrogen Peroxide on a Pt-Metallized 4-Mercaptopyridine Self-Assembled Monolayer on Au(111)

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A systematic investigation of the hydrogen peroxide oxidation reaction (HPOR) on an Au(111) single crystal modified with a Pt metallized 4,4'-dithiodipyridine self-assembled monolayer (SAM) in phosphate buffer (pH = 7.3) has been conducted. While the voltammetric behavior of bare Au shows considerable electrocatalytic activity towards the HPOR, the inhibition of the oxidation reaction after modification with the SAM implies that adsorbed 4-mercaptopyridine molecules do not catalyze the HPOR. However, SAM-modified Au(111) shows a catalytic activity for the HPOR after a single metallization step fabricating Pt islands on-top. Hydrogen peroxide (HP) may then either react at the Pt nanoislands similar to metal nanoparticles deposited on insulating SAMs[1][2] or on the reactivated Au sites, made accessible by disordered structural changes of the SAM induced by the metallization[3] (**Figure *1***). The shape of the voltammetric profiles for the HPOR on repeatedly metallized SAMs suggests that the contribution of Au to the total current density gradually diminishes with increasing Pt coverage while the contribution of the Pt nanoislands increases. The electrochemical behavior is dominated by Pt already at a coverage of 0.5 ML.

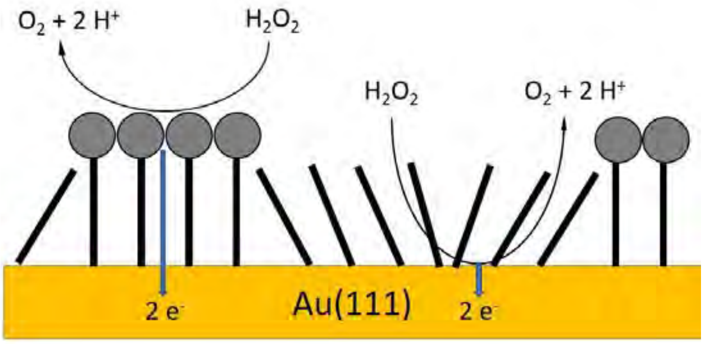

Figure 1: HPOR on a Pt island (grey circles represent Pt atoms) and on the uncovered Au(111) surface. Black bars represent the SAM of 4-mercaptopyridine molecules.

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Composites Based on Three-dimensional Graphene and Transition Metal Dichalcogenides as the Electrode Materials in Supercapacitors

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Supercapacitors are capable of delivering high power density but moderate energy density at the same time. In light of this fact, researchers are endeavoring to intensify the energy density of supercapacitors without deteriorating their power capabilities through designing components with more sophisticated structures. Among various adopted approaches for improving supercapacitors' energy density, integrating high conductivity components such as carbonaceous materials, with faradaic materials, e.g., metal oxides/hydroxides/sulfides, is of paramount importance. Considering different carbonaceous structures, three-dimensional porous architecture based on graphene (3DG) is promising due to various physical and electrochemical features such as structural interconnectivities, lightweight, high active surface area, and unique porosity. Due to excellent mechanical stability, 3DG can serve as a promising substrate for depositing other materials. Among redox-active metallic materials, transition metal dichalcogenides (TMDs) have attracted widespread attention since most of them have a low cost and a high theoretical capacitance. Utilizing both 3DG and TMDs can improve the electrochemical performance of supercapacitors. Here, we demonstrate that combining 3DG with different spinel-type TMDs will give electrode materials that can deliver better electrochemical parameters compared to each single component. 3DG contains a wide range of pores with different diameters from nanometer to micrometer. Therefore, the redox-active material can be easily embedded inside the pores of the substrate. In this state, we may increase the energy density of the electrode material but at the sacrifice of losing its power density. Owing to this fact, electrode material based on 3DG and Co_3S_4 was constructed with different ratios to evaluate the proper proportion of substrate and the redox-active material. In the same line and in separate procedures, the electrode materials based on 3DG, as the substrate, as well as Ni_3S_4 and MnS_2 were synthesized. The prepared electrode materials were characterized by the various textural/structural methods: scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy. For electrochemical characterization, electrode materials with 1 cm diameter and fairly 1 mm thickness were cut and symmetrically served as both positive and negative electrodes inside a Swagelok cell without adding any binder or conductive additive. Whatman paper was cut in a diameter of 12 mm and used as the separator. Before running the electrochemical experiments, the electrode material and the separator were immersed in aqueous electrolyte (6 M KOH) for 24 hr to exchange the water in the pores with KOH. Cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy experiments were carried out on a Biologic potentiostat/galvanostat instrument. The electrochemical tests were performed in the applied potential range of 0 - 1 V.

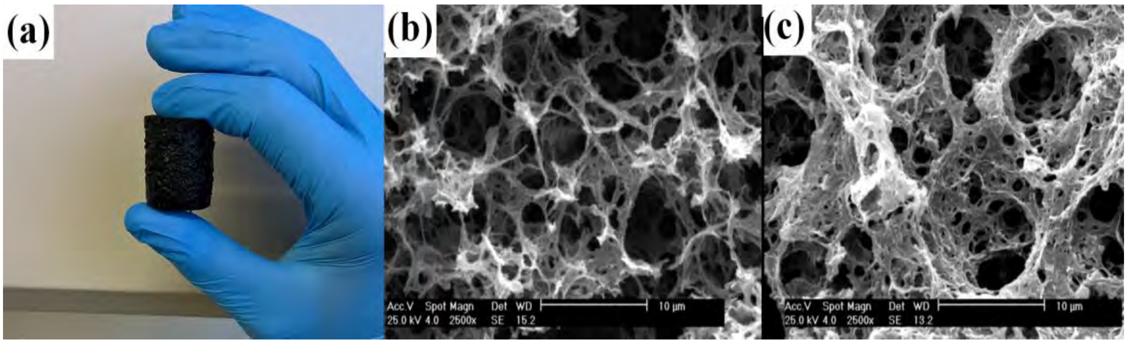

Figure 1. Optical photo of 3DG (a), SEM images of bare 3DG (b) and 3DG/Co_3S_4 (c).

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Investigation on the Long-term Stability of Photosystem 1/Redox Polymer Based Bio-photoelectrodes

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Inspired by natural photosynthesis, great effort has been directed to the design and fabrication of semi-artificial bio-photoelectrochemical devices able to harvest solar energy. Photosystem 1 (PS1), one of the key enzymes that drive photosynthesis, has been increasingly investigated for this aim due to its strong reductive force upon light-induced charge separation processes.

In our previous work, the use of an Os-complex modified redox polymer to wire PS1 with the electrode surface has enabled efficient generation of photocurrents [1]. While O_2 was used as terminal electron acceptor to scavenge the photo-generated electrons, superoxide radicals were formed leading to the generation of partially reduced reactive oxygen species in the surroundings of the immobilized protein complexes, resulting in the inactivation of PS1. In consequence, only a limited long-term stability was observed for the bioelectrode under illumination.

An in-depth evaluation of the PS1/redox polymer-based biocathode was performed by means of scanning photoelectrochemical microscopy, revealing pathways for the generation of oxygen radicals [2]. Thus, in order to prevent the deleterious effects of generated reactive oxygen species, the operation of biophotocathodes under anaerobic conditions is indispensable. The careful selection of an electron scavenger capable of efficient electron extraction even in the absence of O_2 made the operation of the PS1-based photoelectrode with an extensively improved long-term stability possible [3].

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Nonaqueous Zinc-organic Battery with Ultra-long life and Wide Operating Temperature

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Zinc (Zn) metal is an attractive anode material for next generation batteries due to their high theoretical gravimetric and volumetric capacities, abundance, nontoxicity, and cost-effectiveness. [1-3] Rechargeable Zn metal batteries using a mild aqueous electrolyte, which showing promising electrochemical performance, are extracting extensive attention of researchers. [4, 5] This directly drove the recent renaissance of rechargeable Zn battery development, such as Zn//MnO_2, [6, 7] Zn//V_2O_5, [8, 9] Zn//hexacyanoferrate. [10, 11] Unfortunately, the inescapable H_2 evolution and dendrite formation on Zn anode join hands with the structure collapse of host materials in cathode setting an intrinsic limit on the cycle life and the practical of the Zn metal rechargeable batteries.

Herein, we have successfully demonstrated a promising nonaqueous Zn-organic battery, in which the phenanthrenequinone macrocyclic trimer (PQ-MCT) and Zn foil serve as cathode and anode, respectively, while N, N-dimethylformamide (DMF) solution containing ZnTFMS (ZnTFMS/DMF) serves as electrolyte. Its operation depends on the reversible coordination reaction (C=O/C-O-0.5Zn conversion) in cathode and the Zn plating/striping in anode, in parallel with Zn^{2+} transfer in between, showing a rock-chair mechanism. It is found that the formation of Zn^{2+}-DMF complex enable Zn^{2+} uniformly transported to the surface of Zn electrode, facilitating dendrite-free Zn platting. In addition, the aprotic nature of the electrolyte eliminates the issue of undesired H_2 evolution on Zn surface, increasing the reversibility of platting/stripping. Therefore, Zinc anode shows high cycle stability in such electrolyte. Furthermore, owing the insolubility in DMF solution and the high reversibility of coordination reaction, PQ-MCT can serve as a robust cathode with fast kinetics. As a result, such Zn//PQ-MCT full battery exhibits super-long life (20000 cycles) and high power/energy densities. Finally, benefiting from the low freezing point and high boiling point, this full battery even can be operated in wide temperature range of 220 ℃ (from -70 ℃ to 150 ℃).

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Identification of active sites in ultralow-loading PtFe composite ORR catalysts with high utilization

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Cathodic oxygen reduction reaction (ORR) governs overall proton exchange membrane fuel cell (PEMFC) performance. Among all the catalysts available, the Pt-based catalyst is well deserved the best oxygen reduction catalyst, which makes them practically irreplaceable at present. However, a vast amount of platinum (Pt) is required due to the sluggish ORR kinetics, especially in harsh acidic media, which casts a blight on their economic competitiveness and sustainable development. This constraints are pressing incentives for exploring catalysts with high Pt utilization. The most mature alternatives is Pt alloy nanoparticles with substantial enhancement in activity and significant reduction in Pt loading[1]. The electronic structure of surface Pt atoms can be tailored by the so-called geometric effect and ligand effect, which are mainly originating from the lattice mismatch and heterometallic interaction. Here, we synthesized a hollow structured PtFe composite catalysts by acid leaching. The usage of Pt could be reduced without compromising the ORR activity comparing to pure Pt catalysts. Based on a series of control experiments analysis, high-resolution electron microscope image, and CO stripping data[2], we can identify the true active site of this complex catalysts, which possess non-uniform particles after high temperature calcination and acid leaching. The largest contribution to catalytic activity is from the small-sized hollow particles, where the improved ORR activity was due to the weakened oxygen-binding strength induced by the electronic structure of the segregated Pt-skin surface.

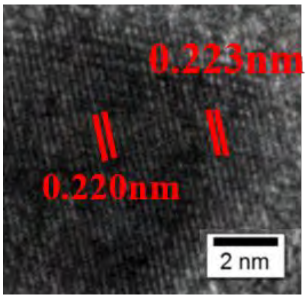

Fig.1 HRTEM of PtFe/C

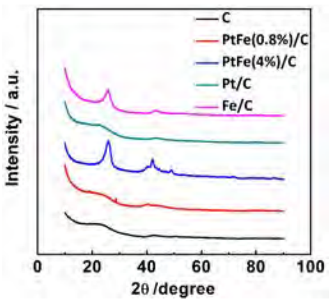

Fig.2 XRD of PtFe/C and reference samples

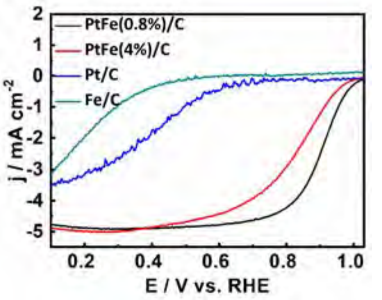

Fig.3 LSV of PtFe/C and reference samples

Acknowledgements
The work was supported by the National Natural Science Foundation of China (21633008, 21875243, 21673220, U1601211), National Science and Technology Major Project (2017YFB0102900), Jilin Province Science and Technology Development Program (20190201270JC, 20180101030JC). Part of the computational time is supported by the High-Performance Computing Center of Jilin University and Jilin Province, as well as Network and Computing Center of Changchun Institute of Applied Chemistry. Prof. Wei Xing thanks Gusu talent program for the financial support.

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Reliable Differential Capacitance from Computer Simulation of Ionic Liquid Confined Between Charged Electrodes

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The electric double layer (EDL) is a region occurring at the interface between two phases, most commonly an electrode and an electrolyte. Differential capacitance has central role in the theories of EDL. First of all, it is one of the few observables that can be directly compared to experimental measurements. Additionally, it describes the magnitude of electrolyte response to the change in applied potential. Finally, the differential capacitance is in the heart of modern technologies such as supercapacitors and batteries [1]. While the basic theory behind the interface between dilute electrolytes and electrodes has been established, the EDL occurring between metal surfaces and concentrated electrolytes, such as ionic liquids, represents a challenge for theory [2,3]. Using a computational approach, the capacitance-potential curve, $C(U)$, for such systems can be derived from molecular dynamics (MD) simulations. Although a differential capacitance for various ionic liquids accessed via MD simulations has been reported in the literature [4,5], retrieving a C(U) curve from the MD trajectories is not trivial. Usually, it implies a differentiation of the charge-potential curve. Independently on MD methodology implemented (i.e., simulation with a constant charge or constant potential applied), the curve fitting is a crucial step, as the resulting differential capacitance strongly depends on the fitting method used and must be manipulated with care.

The present work focuses on the MD simulation data treatment in the process of C(U) curve fitting, however, always taking into account the position of surface charge plane [6]. We consider various simulations techniques and approaches for the treatment of simulation data. We demonstrate that the shape of the capacitance curve is largely determined by the electronic structure, which agrees with previous experimental results [7]. A more detailed analysis provides insights towards potentially useful combinations of electrode and electrolyte, capable of yielding significantly higher capacitances that are required for advanced electrochemical devices.

Acknowledgements. This work was supported by Projects UID/QUI/50006/2020 (LAQV@REQUIMTE) and UID/QUI/00081/2020 (CIQUP) with funding from FCT/MCTES through national funds. The study was also supported by the Estonian Research Council (grants IUT20-13, PSG249, and PUT1107) and the European Regional Development Fund (grant TK141).

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Glucose Sensing Electrode Fabrication using Unnatural Amino Acid Incorporated and Ferrocene Conjugated GDH

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Electrochemical enzymatic glucose sensors measure glucose concentration through a current generated by an enzyme specifically oxidizing glucose. However, the cofactor in which this reaction occurs is buried inside the macromolecule of the enzyme, the efficiency of electrons transferred to the electrode surface is very low. Therefore, the method of coating the electrode surface using various linkers to crosslinking the glucose oxidizing enzyme and the redox polymer that assists electron transfer is frequently applied. In this study, we use the modified enzyme to fabricate the glucose sensor which is possible to direct electron transfer, without using a separate mediator and cross-linking process. An azide group was introduced on the surface of glucose dehydrogenase through the genetic incorporation of an unnatural amino acid, then a small molecule of ferrocene containing alkyne combines on the surface of GDH through the “click” reaction. The electrode was simply prepared by drop-coating the modified enzyme on the screen printed carbon electrode, dried in room temperature. We measured the glucose in a range of 0.1~1.0 mM in PBS solution, used the electrode prepared above as working electrode, Pt wire as counter, Ag/AgCl as reference. The results proved that the direct electron transfer efficiency was clearly improved compared to the electrode using an enzyme of a natural structure with no modification. Enzyme activity in each process was also observed and compared to that of natural structures.

Elucidating the Mechanism of Li Insertion into $Fe_{1-x}S$/Carbon via in Operando Synchrotron Studies

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The detailed understanding of kinetic and phase dynamics occurring in lithium-ion batteries (LIBs) is crucial for their further improvement. We previously reported that $Fe_{1-x}S$/C nanocomposite shows a promising performance as anode material for LIBs. However, the underlying lithium storage mechanism was not entirely understood during the 1st cycle. In this work, we apply *in operando* nondestructive synchrotron X-ray diffraction (SRD) and X-ray absorption spectroscopy (XAS) to directly track the complex electrochemical reaction mechanisms during the 1st (de)lithiation processes in the $Fe_{1-x}S$/C nanocomposite. The combination of *in operando* techniques enables the uncovering of the pronounced electronic changes and structural alterations on different length-scales. Additionally, the investigation of kinetics processes, morphological changes and internal resistance dynamics are discussed. These results reveal that the phase transition of $Fe_{1-x}S \rightarrow Li_2Fe_{1-x}S_2 \rightarrow Fe^0+Li_2S$ occurs during the 1st lithiation process. The redox reaction of $Fe^{2+} \rightarrow Fe^0$ is confirmed by *in operando* XAS. During the 1st (de)-lithiation process, Fe^0 and Li_2S convert to $Li_{2-y}Fe_{1-x}S_2$ and Li^+ is extracted from the Li_2S to $Li_{2-y}S$ phase. The phase transition from Li_2S to $Li_{2-y}S$ is not detected in previous findings. After the 1st de-lithiation process, amorphous $Fe_{1-x}S$ nanoparticles are embedded within the remaining Li_2S matrix[1-3].

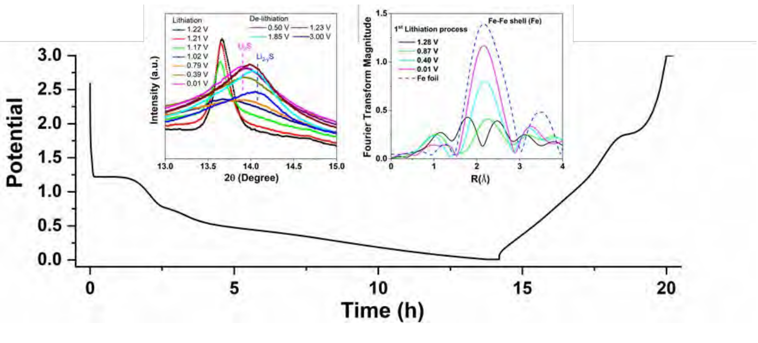

Fig. 1 In operando XRD and XAS of $Fe_{1-x}S$/C *during the 1st lithiation and de-lithiation processes.*

Acknowledgments:

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Molecular Dynamics Simulation of Ionic Liquid at Electrified Interface: Impact of Electrode Surface Crystallography

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Recent progress in the application of ionic liquids (ILs) as electrolytes in supercapacitors, Li-ion batteries, and actuators [1] has stimulated studies of the electrical double layer (EDL) in this media [2], as the EDL structure affects the performance of all listed electrochemical devices. Due to a strong anion–cation interaction in ILs, the ionic layering near the surface is induced [3], resulting in an alternatively charged ionic structure (see Figure 1). To calculate the capacitance-potential dependence, $C(U)$, in such complex systems, advanced theoretical models are being developed along with numerous computer simulations [4,5]. In general, with the focus on the electrolyte side of the EDL, different models give two types of C(U) curves: with one (bell-shaped) or two (camel-shaped) maxima near the potential of zero charge [5,6]. In this molecular dynamics (MD) study, we show the correlation between the electrode surface corrugation in conjunction with the electrolyte atoms sizes and the shape of the $C(U)$ curve. For this reason, we chose well-studied 1-butyl-3-methylimidazolium hexafluorophosphate (BMImPF$_6$) IL and three charged gold surfaces, namely, Au(111), Au(110), and Au(100). Special attention is paid to the effect of surface crystallography on the calculated C(U) dependence in reference to the experimental data.

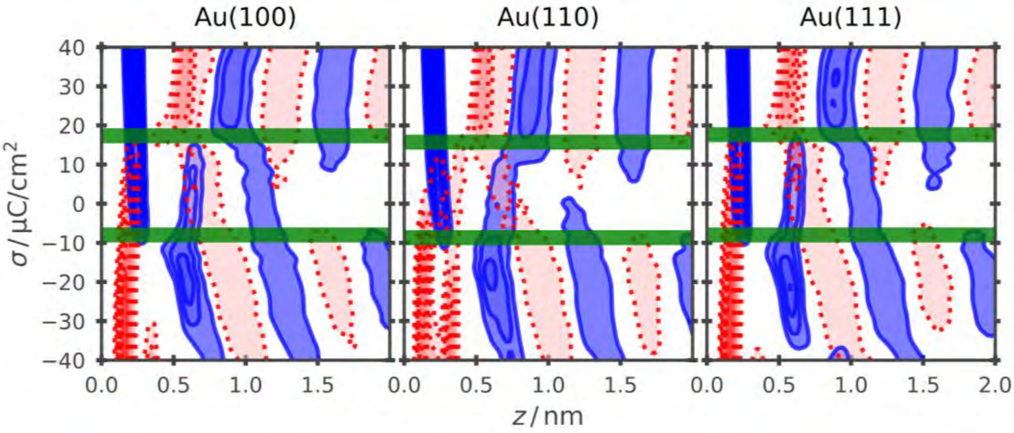

Figure 1: Ion number density contour plots on the electrode's surface. The cation (red) – anion (blue) layering structure is visible, especially at high electrode charges (in the top and bottom of green lines).

Acknowledgements. This work was supported by Projects UID/QUI/50006/2020 (LAQV@REQUIMTE) and UID/QUI/00081/2020 (CIQUP) with funding from FCT/MCTES through national funds. The study was also supported by the Estonian Research Council (grants IUT20-13, PSG249, and PUT1107) and the European Regional Development Fund (grant TK141).

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Cyclic Voltammetry is invasive on a Bioelectrochemical Systems

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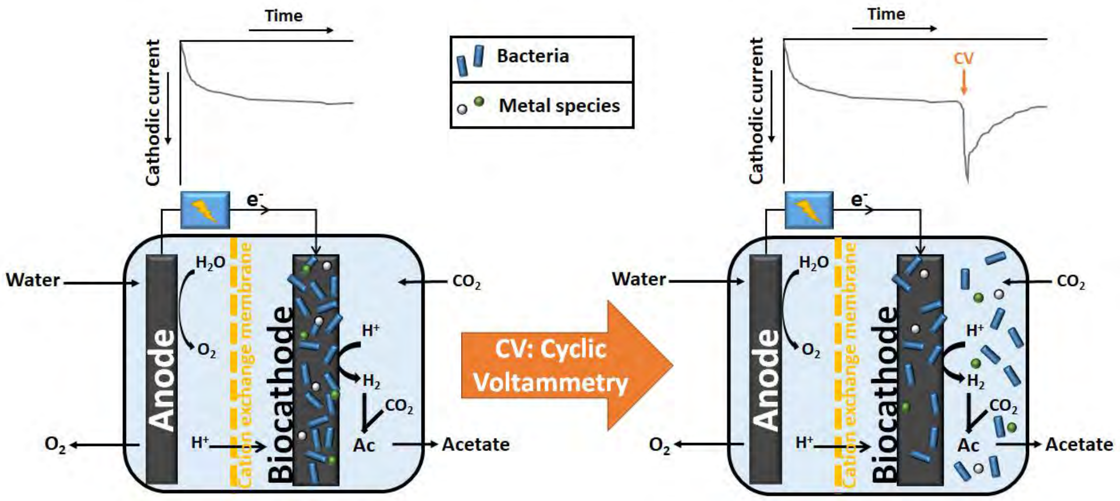
In general electrochemical characterization techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy are regarded as non-invasive techniques. Here we show that non-invasiveness does not simply account for the application of cyclic voltammetry (CV) on a bioelectrochemical system. This finding requires a rethinking on the usefulness of CV on bioelectrochemistry. CV is widely used in bioelectrochemstry to measure biocatholytic activity, electrode composition or reaction kinetics. Although CV is considered to be an innocent technique, a recent study from Jourdin, et al. [1] showed that the cathodic current of a bioelectrochemical CO_2 reduction system increased after a CV scan was performed on the system. This finding led to the objective of our study, to study the effect of CV on microbial electrosynthesis. A bioelectrochemical system was developed with a mixed culture biofilm in which CO_2 was elongated to acetate. The effects of CV on both reactor performance and biocathode composition were studied. CV repetitively enhanced current density for up to 20 days. Additionally, a different oxidation peak was observed during the first cycle of the CV scan compared to the subsequent two cycles. This indicated that a different oxidation reaction occurred during the first cycle compared to the subsequent two cycles. To further investigate this change, the metal composition of the biocathode was studied. The concentrations of Fe, Co, Al, Ba, Mn, Mo and biomass increased in the biotic catholyte predominantly during the oxidation peak of the first CV cycle, indicating these compounds were released from the cathode. The biocatholyte concentrations of the released metals were still increased at the end of the CV, they decreased rapidly within four hours after the CV at the cathodic operation potential of -0.85 V vs SHE.

The results from this study show that CV is not simply an analysis technique, but causes changes at the biocathode. Invasiveness of CV on other bioelectrochemical systems should be investigated to understand the potential impact of this technique. Present findings are potential applicable to modify or provide in-situ maintenance on biocathodes. Moreover, our findings form a starting point for follow up studies investigating the mechanisms behind the possible catalytic effects of the performed analysis method.



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NIR-Emitting Organic-Inorganic Ureasil-based Hybrid Electrolytes for Electrochromic Devices

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Energy consumption in residential and commercial/office buildings has a significant impact on the environment, contributing significantly to greenhouse gas emissions and global warming. Not surprisingly, energy efficiency has become a priority target for the energy policies in many countries. The emerging concepts of zero and nearly-zero energy buildings call for new materials and new technologies. In this context, the interest in the development of smart electrochromic windows (ECWs), enabling the fine control of the incident solar spectrum (heat (near-infrared (NIR) region) and sunlight (visible region)) has grown significantly in the last few years [1]. Such windows rely on electrochromic devices (ECDs). ECDs undergo a reversible color change upon application of a small voltage (1-3 V). Their archetypal configuration comprises a multilayer structure: an EC film of the cathodically coloring tungsten trioxide (WO_3), an electrolyte film, an EC film of the anodically coloring nickel oxide (NiO), and two outermost transparent conductive oxide (TCO) layers, such as visible-transparent-indium tin oxide (ITO) [1], or visible- and NIR-transparent amorphous indium zinc oxide (a-IZO) [2(a)].
Aiming the production of NIR-emitting smart ECWs providing additional indoors human comfort in buildings, electrolytes doped with erbium salts and/or complexes [2 (a-b)] were reported. Herein we used the sol-gel method [2(b)] to prepare transparent and thin films resulting from the co-condensation of two urea cross-linked poly(oxyethylene)/siloxane matrices: a di-ureasil d-U(Y) [3] and a tri-ureasil t-U(Y') [4], where Y=600, 900, 2000 and Y'=400, 3000 and 5000 represent the average molecular weight of the polymers chains. The t-U(Y') materials were doped with a commercial ionic liquid, and the d-U(Y) matrices were doped with erbium complexes. For comparison purposes non-doped matrices were also prepared. ECDs incorporating optimized electrolytes were assembled and their electro-optical performance was evaluated.

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Spectroelectrochemistry of Nonunity Stoichiometry Electrode Reactions: A Theoretical Study

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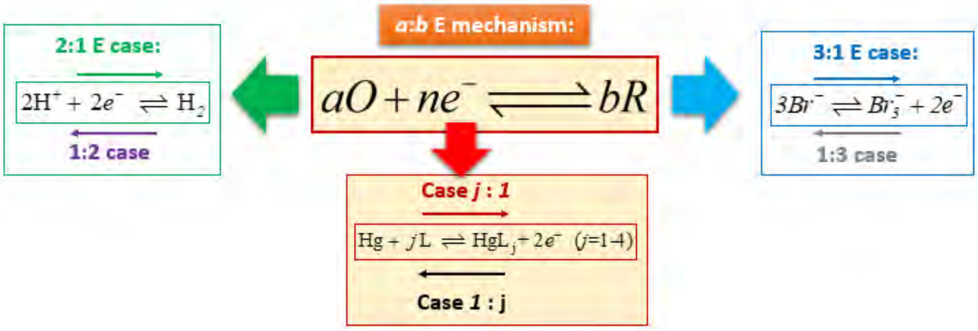
Key electrochemical processes are reported to follow non-unity stoichiometries in a variety of scientific and technological fields [1]: energy storage and conversion (*eg*., halides in dye-sensitized solar cells, hydrogen production), environmental monitoring and assessment (*eg*., mercury complexes) and electrosynthesis (*eg*., dimerization of the electrode product), among others (see *Scheme* I).



Scheme I. Schematic and examples of electrochemical reactions with nonunity stoichiometry.

The full characterization of this kind of processes can be challenging considering the number of parameters to be determined, at least: the stoichiometric and diffusion coefficients of the redox species, the number of electrons transferred, and the formal potential of the couple O/R. Hence, as in other contexts [2,3], the joint analysis of simultaneous electrochemical and spectroscopic measurements can be advantageous for comprehensive and sound studies.

Attending to the above, a general theoretical treatment is developed in this work to model the spectroelectrochemical response at macroelectrodes of reversible electrode reactions with complex stoichiometry *a:b* (see *Scheme* I). The theory is applicable to any voltammetric perturbation and whatever the diffusion coefficient and bulk concentration of the redox species. Simple equations are derived for the current-potential response, surface concentrations and concentration profiles of the most common 2:1, 1:2, 3:1 and 1:3 cases. From the theoretical solutions obtained, the value of spectroelectrochemistry is assessed in the elucidation and quantitative characterization of the reaction stoichiometry. Thus, the voltabsortometric and chronoabsortometric responses are investigated both in normal and parallel modes, establishing suitable experimental approaches, diagnosis criteria and protocols for data analysis.

Acknowledgements

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Chemically Modified Electrodes Based on Methylene Blue and SBA-15 composites

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The aim of the present work is to assess and develop chemically modified electrodes based on a composite formed by Methylene blue (MB) and a mesoporous ordered structured (SBA-15) [1,2].
Methylene blue could be a mediator, which acts as electrocatalyst in certain redox reactions (e.g. detection of cancer markers). In addition, Methylene blue is a disinfectant and an antioxidant. It also is an antidote in case of intoxications by nitrates (NO_3^-), nitrites (NO_2^-) or chlorates (ClO_3^-) [3].
The preparation of the modified electrode was realized by drop-casting method, followed by evaporation of the solvent after deposition of a solution containing MB and SBA-15 on a glassy carbon surface. The obtained composite layer was protected by a Nafion film.
The GC/SBA-15-MB/Nafion modified electrode will be characterized by electrochemical methods of investigation (cyclic voltammetry and square wave voltammetry) in order to obtain the electrochemical parameters (ΔE, Eo', Ipa/Ipc, FWHM (full width at half maximum)). The influence of the experimental conditions (scan rate and pH) on the electrochemical behavior and the stability of the GC/SBA-15-MB/Nafion modified electrode will be investigated. Also, the morpho-structural characterization will be evaluated by Atomic force microscopy, AFM; Energy-dispersive X-ray spectroscopy, EDX and Scanning Electron Microscopy, SEM.
The GC/SBA-15-MB/Nafion modified electrode will be tested for H_2O_2 detection.

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Scale-up Effect on Performance of Reversible Chlor-Alkali Electro-Absorption Cells

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Nowadays, because of global warming, use of renewable energies has become of a paramount importance. Europe and other countries all around the world are putting a great effort on the introduction of the renewable energies (e.g. solar and wind energies) in the electricity grid but there are still some inconveniences that limit their implementation such as the capital costs and their intermittent nature. To overcome the last one, a storage medium or energy carrier is needed. It is in this scenario where the hydrogen technology plays a very important role as it can be stored and produced from primary energy sources [1]. Flow batteries based on hydrogen-halogen compounds have generated interest to different researchers as renewable energy storage systems [2]. Because of relatively facile chlorine redox kinetics, H2-Cl2 cells are capable of operation with lower activation loss associated to the chlorine electrode compared with the sluggish oxygen reduction reaction of the H_2-O_2 based fuel cells.

The fuel cell and the electrolyzer operation modes can be carried out in the same electrochemical cell and with the same electrodes. Thus, a reversible electrochemical cell can be operated as electrolyzer or fuel cell depending on the reagents that are fed into the electrodic compartments. It allows the use of a single equipment for the storage of energy as chemicals. Thus, in a reversible cell, the same electrodes are used in both operation modes, so they must show good performance when acting as anodes or cathodes, because they are going to perform in both roles. For hydrogen oxidation, platinum is known to be a very good electrode. For chloride oxidation, Mixed Metal Oxides (MMO) based on RuO_2 are the most widely used electrodes [3]. It is interesting to assess the performance of both types of electrodes when they are used in the reduction of chlorine and protons to produce hydrogen.

In this work, the performance of a reversible electrochemical cell for the storage of energy using the chloralkaline process was investigated. In a first stage, we checked that the anode composition (Ru/Pt ratio) influences in the performance of the reversible cell. It was found that a molar ratio Ru:Pt within the range 3-4 was good enough to obtain a good performance in both operation modes [4]. In the second stage, different models or configuration of cells are tested. Results demonstrate that design of the cell has a superb significance on the performances obtained [5]. Based on these results, we used a cell larger than the first cell we designed, in order to check the performance of the reversible cell at different scales. We observed that the results in both cells were similar, and in the scaled-up fuel cell, the influence of applied (from 25 to 80 ºC) temperature is more relevant.

These results demonstrate that working with larger cells while maintaining the efficiency of the process is possible

Acknowledgements

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In Search of the Best Operation Conditions for the SO_2 Electrolysis at High Temperature (Above 100 °C)

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The Hybrid Sulphur Cycle has been identified as a highly efficient method for large-scale hydrogen production. Based on this cycle, this work is related to the step where SO_2 is electrochemically oxidized in the anode to form sulphuric acid, protons, and electrons ($E^0 = 0.17$ V vs SHE). The protons are conducted across the electrolyte separator to the cathode where they recombine with the electrons to form H_2 according to equations 1 and 2.

$$SO_2\,(aq) + 2\,H_2O \rightarrow H_2SO_4\,(aq) + 2H^+ + 2\,e^- \qquad (1)$$

$$2H^+ + 2\,e^- \rightarrow H_2(g) \qquad (2)$$

For high cycle efficiencies, operating at temperatures higher than 100°C in the electrolyzer is recommended. However, SO_2 depolarized electrolysis is currently mostly studied using Nafion membranes which limits the operating temperature to around 80°C because of the need of hydration of these membranes. That is the reason for the need of developing new materials for this application. PBI based membranes are a promising alternative for working at high temperatures due to they do not need to be humidified for its operation at high temperature, also the degradation temperature of this polymer (ca. 500°C) makes it suitable for this application.

A commercial PBI membrane supplied by Danish Power Systems USA was used for the experiments. The membranes were doped with 85 wt% phosphoric acid. As reactants for the electrolysis, MiliQ water and SO_2 were used. A platinum loading of 0.7 mg Pt/cm^2 was employed on both electrodes (anode and cathode) using 40% Pt/Vulcan carbon XC72 as catalyst by spraying a catalytic ink on the electrode surface. For the electrochemical measurements, a potentiostat/galvanostat (AUTOLAB, Netherland) equipped with Frequency Response Analysis (FRA module) was used.
The tests were performed in a 25 cm^2 SO_2 depolarized electrolysis cell based on PEMFC technology, working with SO_2 in gas phase and generating steam which will be mixed with the SO_2 flow. The performance was studied in a range of temperatures from 120°C to 150°C. Polarization curves were obtained by scanning the applied potential from 0.00 to 1.00 V (vs RHE) at a scan rate of 10 mV s^{-1}. Impedance spectroscopy was measured potentiostatically, at 0.15 and 0.55 V, with a perturbation signal of 10% with a frequency range of 10 kHz to 100 mHz
Results showed that increasing temperature has not always a beneficial effect on the performance of the electrolyzer as result of enhancement of parasitic reactions. On the other hand, when an inert gas is introduced to the cathode of the cell it results in some advantageous effects as they can remove the possible SO_2 which has crossed the membrane. Regarding this aspect, nitrogen and a mixture of nitrogen and steam where studied as feed for the cathode. Finally, the effect of the flows of water and sulfur dioxide in the anode where also studied in order to evaluate the optimum stoichiometry of the system.

ACKNOWLEDGEMENTS
Financial support from the Junta de Comunidades de Castilla-La Mancha and the FEDER –EU Program, Project ASEPHAM. Grant number “SBPLY/17/180501/000330” is gratefully acknowledged.

Development of a Sensitive Electrochemical Paracetamol Sensor based on Nano-composite Fe_2O_3/TiO_2 Electrodes

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Paracetamol's usage, a widely used analgesic and antipyretic drug, suffers from overdoses and chronic usage problems and its concomitant use with alcohol or other drugs causes toxic metabolite accumulation, hepatic toxicity and disorders, nephrotoxicity, pancreas inflammation and skin rashes. Therefore, accurate determination of paracetamol is necessary during quality control in pharmaceutical formulations and biological fluids.

Paracetamol is an electrochemically active structure which is oxidized on various electrodes, while on bare electrode this occurs at high overpotentials. Chemically modified electrodes have been used successfully in order to lower the oxidation overpotential and increase the current sensitivity without affecting the drug concentration determination.[1]

In this work, nanocomposite electrodes of hematite (α-Fe_2O_3) deposited on mesoporous TiO_2 film electrodes on ITO glass were found to be simple, low cost, sensitive, electrochemical paracetamol sensors, with improved conductivity compared to bare TiO_2 films.[2-4] The electrodes' excellent electrochemical behavior was examined by cyclic and differential pulse voltammetry, while their structure was investigated by FESEM, EDS and X-ray diffraction. Under optimized conditions these electrodes demonstrated excellent electrocatalytic activity towards paracetamol oxidation in the linear response concentration range from 2 to 40 μM (correlation coefficient 0.987) with a 1.07 μM detection limit. These sensors demonstrated good repeatability, reproducibility and stability, applicable for pharmaceutical paracetamol determination.

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Electroactive sulfate reducing microorganisms and their relevance in accelerated iron corrosion

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Sulfate-reducing microorganisms (SRM) are major metabolic groups of microorganisms causing microbially influenced corrosion (MIC) and known for their corrosivity through the formation of biogenic hydrogen sulfide (H_2S), iron sulfide (FeS), and hydrogenotrophic metabolism (1,2). Among these distinct corrosion mechanisms of MIC, electromicrobiologically influenced corrosion (EMIC) is currently recognized as being involved in the acceleration of the iron corrosion (3). Recent research has shown the importance of electroactive SRM (ESRM) and their role in possible ennoblement and accelerated corrosion of iron structures due to their special adaptations of extracellular electron uptake mechanisms through iron oxidation (4, 5). Such studies indicate that ESRM influences the cathodic reaction of iron corrosion. In the present study, we review such abilities in known corrosive bacterial genera of the families, *Desulfovibrionaceae* and *Desulfobulbaceae* to use iron structures as a sole source of electron and explore its electron uptake mechanisms in relevance to EMIC. These specialized bacterial species employ different strategies including cell-associated direct electron uptake through outer-membrane vesicles (6,7), formation, and accumulation of electrically-conductive mineral crusts (FeS) through dissimilatory sulfate reduction (2,8) and redox mediators' generation from bacterial cells (9). Nevertheless, the new electromicrobiological routes of such corrosive behavior have yet to be studied. Since the microorganisms are adapted to acquire energy from various environments, further exploring the research on extracellular electron uptake mechanisms will provide novel insights into microbial evolution and energy conversion besides its technical relevance.

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How to Measure Sustainable Electrical Power Produced by Thermogalvanic Cells using Waste Heat

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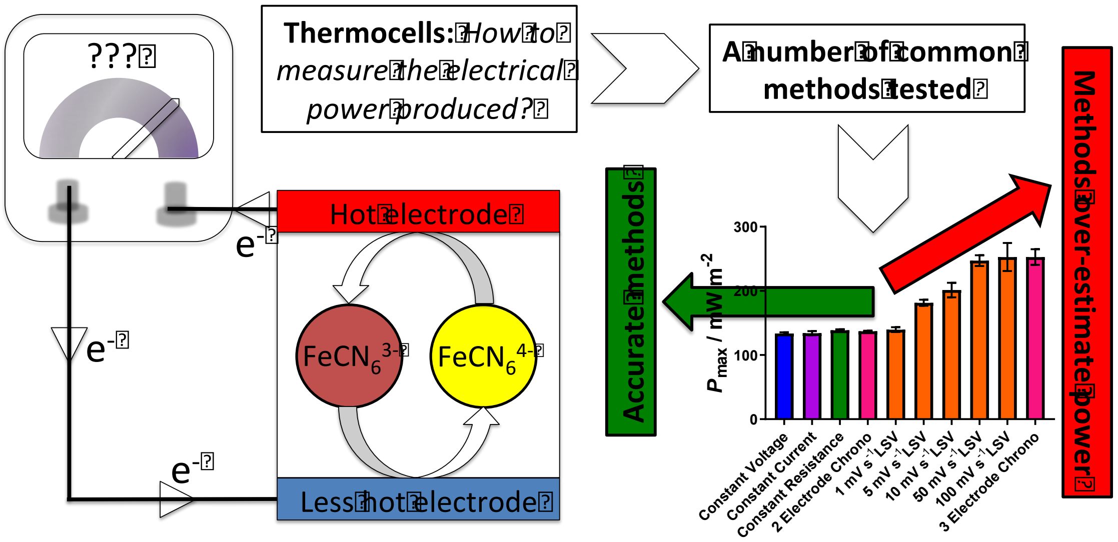
Thermogalvanic cells can exploit a temperature gradient (*e.g.* from waste heat) to generate electrical power. This is driven by the entropy difference between two redox states (commonly observed in electrochemistry as *the temperature coefficient of the reduction potential*).[1] This is exemplified in the cartoon below, for water containing 0.2 M of $K_3[Fe(CN)_6]$ and 0.2 M of $K_4[Fe(CN)_6]$. With two electrodes sharing an electrolyte containing both redox states, redox processes and mass transfer ensure a continual flow of electricity (as long as the temperature difference persists).[2]

Numerous thermogalvanic devices (or thermocells) using novel cell designs,[3] electrolytes,[4] redox couples,[5] *etc.* are now being published, and invariably compared. But are the comparisons – and even the initial measurement and characterisation – valid?

This poster will summarise recently published work[6] where a 'round robin' type approach was made to comparing 5 common methods reported in the literature for characterising the electrical power produced by thermogalvanic cells. As summarised in the Figure below, some methods were accurate and some significantly overestimated the power capable of being sustainably produced. Normalisation of power values are also increasingly common, given the wide range of temperatures different groups apply, culminating in the popular adoption of "temperature-insensitive figure of merit for areal power density". This method of normalisation was explored, and found to be significantly temperature-sensitive; an alternative method of normalisation was also demonstrated.



Thermocells: *How to measure the electrical power produced?*

A number of common methods tested

Accurate methods

Methods over-estimate power

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Controlling proton-electron transfer in CO reduction electrocatalysts

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CO_2-derived fuels, synthesized using renewable energy, present an attractive way towards a sustainable energy system. Impressive progress has been achieved in the production of CO and formic acid from CO_2. The selective electrosynthesis of higher order products such as ethylene and methane remains challenging, however. This can be attributed to an insufficient understanding of the complex reaction networks involved in transferring multiple protons and electrons to surface-bound intermediates.

To shed light into this fascinating maze, I will present investigations into the electrochemical reduction of CO in nonaqueous model systems, allowing the independent interrogation of the role of proton donor pKa, solvent, cation nature and molecular structure and the interaction of conjugate base anions with the electrode surface.

Our experiments explain the kinetic bifurcation between methane and ethylene production and provide an integrated mechanistic picture that explains why these pathways are either affected or not by the nature of electrolyte cations. I will show, how these results can be exploited to modulate the catalytic selectivity between methane, ethylene and parasitic hydrogen.

Ammonia Modified Graphene Oxide – Gold Nanoparticles Composite as a Sensing Platform

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Graphene oxide (GO) is a novel material which is an important member of graphene family. The popularity of GO originates from the combination of pristine graphene features such as exceptional mechanic, electronic and thermal properties and advantages of oxygen surface groups. GO contains many oxygen groups in its structure, including epoxide, hydroxyl and carbonyl moieties, which help to overcome some limitations of pure graphene, such as high hydrophobicity, poor solubility in aqueous solvents and difficulties in surface functionalization [1]. Due to mentioned facts GO is commonly used as a component in many fields, for example in designing electrochemical [2,3] and SERS [4] sensors, catalysis [5], and many more.

GO is a versatile and easy processing material, which can be easily modified by chemical reactions. Presence of various oxygen groups facilitates numerous modifications of GO surface. Increasing attention is devoted to fabrication hybrid nanocomposites, which include graphene oxide and metal nanoparticles [6]. Thanks to imperfect carbon plane of GO and presence of oxygen moieties it is relatively easy to promote efficient adsorption of nanoparticles on its surface. Moreover, presence of graphene oxide is additionally advantageous as it protects nanoparticles from ambient environment and thus prevents from their degradation [7,8].

In this work we have performed a modification of graphene oxide with ammonia solution. Obtained product was thoroughly examined using spectroscopic (Raman, XPS, FTIR, UV-VIS) and microscopic techniques and used as a component of hybrid composite with gold nanoparticles (AuNPs). Hybrid composites consisting AuNPs and as-prepared or modified GO were used as platforms towards electrochemical detection of H_2O_2 and SERS platforms towards optical detection of aromatic dye, rhodamine 6G.

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Development of Lithium-rich $Li_2Mn_{1/2}Ti_{1/2}O_2F$ as cathode material for Li-ion batteries

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As being the bottleneck in the design of advanced Li-ion Batteries, the development of cathode materials remains as a hottest research topic. Low cost and low toxicity make Manganese and Titanium particularly desirable materials for cathode. In this work lithium-rich cathode with the partial substitution of fluorine for oxygen and based on Lithium, Manganese and Titanium was prepared and characterized.
$Li_2Mn_{1/2}Ti_{1/2}O_2F$ (LMTF) has been synthesized using two different approaches: 1) One pot ball mill synthesis starting from the mixtures of all precursor salts according to the stoichiometric ratio (LMTF1) [1]; 2) Combination of a sol-gel first step to synthesize the mid-product $LiMn_{1/2}Ti_{1/2}O_x$ (LMT), then a ball mill step of LMT prepared by sol-gel step and LiF as precursors [2] to obtain LMTF2. The two methods have been optimized changing the ball mill time and speed. $LiMn_{1/2}Ti_{1/2}O_2$ was also synthesized using the ball mill approach as control.
All the samples have been characterized by X-ray diffraction (XRD), Thermal Analysis (TGA, DTA), and Scanning Electron Microscopy (SEM). In fig.1 XRD diffraction patterns of the samples obtained with the different procedures are reported together with the theoretical pattern, as reference. In both cases a disordered-rocksalt structure was obtained indicating the success of the both procedures in the preparation of $Li_2Mn_{1/2}Ti_{1/2}O_2F$ [1].
Furthermore the electrode preparation has been optimized in terms of binder (Polyvinylidene difluoride (PVdF) and Polytetrafluoroethylene (PTFE)) and ratio of components (active material:carbon:binder).
Electrochemical characterization was carried out in Li-ion half cells using Cyclic Voltammetry (CV), and Galvanostatic Cycling with Potential Limitation (GCPL) techniques, pointing at the possible applicability of the prepared LMTF in lithium batteries.

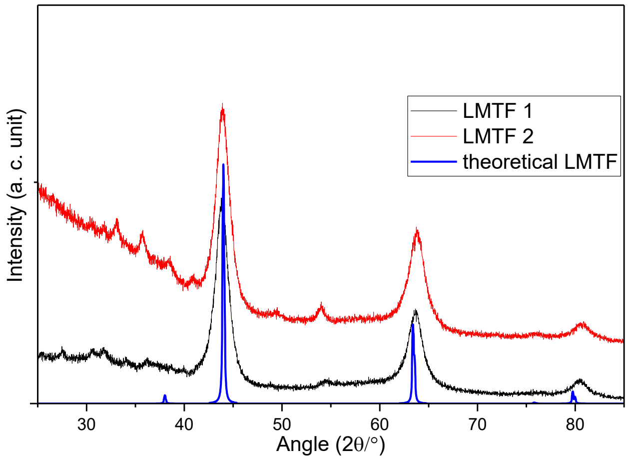

Figure 1. XRD patterns of $Li_2Mn_{1/2}Ti_{1/2}O_2F$ from different approaches

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Electrochemistry of the Calcium Channel Blocker Lercanidipine at a Carbon Black Modified Glassy Carbon Electrode

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Hypertension is one of the main risk factors of cardiovascular diseases, and occurs mainly at the aging population, causing a high number of premature deaths. The use of antihypertensive drugs is important to avoid cardiovascular illness and mortality, and the most important drugs, such as diuretics, calcium antagonists, β-blockers and others, are efficient in the blood pressure control. Lercanidipine is a third generation calcium channel blocker belonging to the dihydropyridine group of compounds, and is used to treat mild to moderate hypertension, chronic stable angina pectoris and Raynaud's syndrome.

The need for rapid, easy and low cost detection, and quantification of pharmaceutical compounds in pharmacological compositions, combined with the necessity of reducing the utilization of organic solvents due ecological considerations, are causing an increasing interest on voltammetric methods that are highly sensitive. The carbon black (CB) nanomaterial was used in many electrochemical studies, due to its interesting properties, that include high conductivity, chemical stability, large surface area, and very low cost.

The lercanidipine electrochemical behaviour at different carbon electrode materials, in a wide pH range, was studied using cyclic, square-wave and differential pulse voltammetry [1]. A comparison was made between unmodified glassy carbon electrode (GCE) and boron doped diamond electrode (BDDE), and GCE and BDDE modified with a CB nanoparticles embedded within a dihexadecylphosphate (DHP) nanostructured film (CB–DHP/GCE and CB–DHP/BDDE). The lercanidipine oxidation, for $3.4 < pH < 9.5$, was pH-dependent, diffusion-controlled, irreversible, and took place at the N1 and C4 positions from the 1,4-dihydropyridine ring. Two consecutive steps were observed, each involving the transfer of one electron and one proton. For $pH > 9.5$, both oxidation processes were pH-independent, and a $pKa = 9.40$ was determined. The lercanidipine reduction was irreversible, and the lercanidipine reduction products were also electroactive, following a reversible electron transfer reaction.

Based on the lercanidipine oxidation, and with no need for N2 purging, the lercanidipine electroanalytical determination at a nanostructured GCE modified with a CB–DHP film (CB–DHP/GCE) was achieved, showing a detection limit of 0.058 μM (3.58×10^{-5} g L^{-1}) and a quantification limit of 0.176 μM (1.08×10^{-4} g L^{-1}), more than ten times lower than previous described.

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Ni/Co-layered Double Hydroxide Anchored on TiO_2 Nanorod Arrays with Enhanced Water Photo-oxidation Performances

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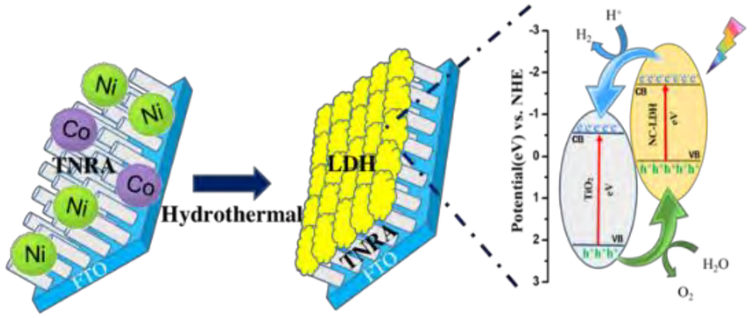
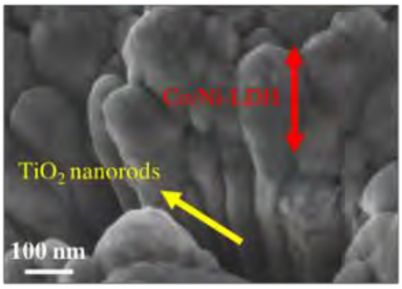
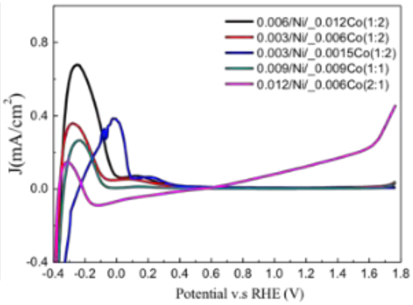
Water splitting photoanodes made of Ni/Co-layered double hydroxide (LDH) anchored at the surface of TiO_2 nanorods array (TNRA) were successfully fabricated by using a two step hydrothermal method, in order to enhance the performances during water photo-oxidation. Ni and Co were selected because of their known activity towards the oxygen evolution reaction (OER). Several experimental parameters have been tuned to maximize the OER efficiency of these NC-LDH@TNRA photoanodes: the nickel-to-cobalt ratio, the thickness and porosity of the coating, and the structure of the interface between TiO2 nanotubes and the active LDH phase. The LDH coatings have galleries containing Co and Ni cations that have been partly oxidized to higher valence states. A current density of 0.45 mA/cm^2 was measured at 1.75V (v.s RHE) in 0.1M Na_2SO_4 neutral electrolyte using a NC-LDH@TNRA photoanode with a 2:1 (Ni : Co) ratio. The OER activity was significantly increased compared to bare TNRA. Based on these results, it is expected that these nanostructured NC-LDH@TNRA photoanodes can provide a new pathway for the fabrication of efficient water photoanode materials and the development of water photo-dissociation devices.







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Electroplating of 3D Printed Electrodes for Selective Electrochemical Reduction of CO_2

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With the rapid development of novel advanced materials for 3D printing, the applicability of these techniques has extended into various specialized fields. In electrochemistry, there is a growing interest in developing printable conductive composite filaments[1,2,3] to be used as electrode materials as an alternative to conventional carbon or metal electrodes. In this work, we chose a commercial polylactic acid/carbon nanotube (PLA/CNT) filament to manufacture electrodes employing fused deposition modeling (FDM) 3D printing process (Fig. 1A) with the goal of developing customized catalysts for the electrochemical reduction of CO_2. In addition, we employed FDM to fabricate an insulating electrode casing from unmodified PLA to ensure a defined area of the electrode/electrolyte interface (Fig. 1A). It is known from the literature that different metals lead to various products of the CO_2 electrochemical reduction.[4] Therefore, we additionally designed and manufactured a PLA cell dedicated for functionalization of electrodes by metallic electroplating (Fig. 1A) to control the product selectivity of CO_2 reduction by selecting a suitable metal ion solution (Cu^{2+}, Sn^{2+} Sn^{4+}, Zn^{2+}, Ag^{+}). Our recent work[3] has demonstrated that metallic electroplating additionally leads to a drop of the kinetic intrinsic barrier for the interfacial electron transfer. Electron transfer properties were investigated by cyclic voltammetry employing $[Ru(NH_3)_6]^{3+/2+}$ couple as the electroactive probe (Fig. 1C). For PLA/CNT electrodes functionalized by potentiostatic electroplating performed in 0.1 M $Cu(NO_3)_2$ for 32 minutes at 6 V, the separation of faradaic maxima decreased and the faradaic peak current distinctly increased. This observation confirms that the Cu layer reduces the kinetic barrier to electron transfer and also increases the total area of surface active sites available for this process. Such an improvement in electrical properties offers great potential for practical use of 3D printed electrodes modified by electroplating such as the production of hydrocarbon chemicals and fuels.

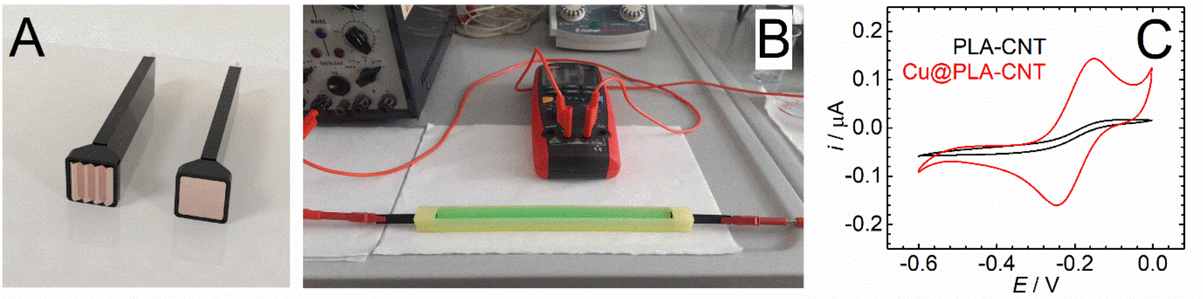

Fig. 1 (A) CAD design of 3D printed electrodes in insulating casing, (B) setup for electroplating of electrodes with controlled applied voltage and recorded resulting current, (C) cyclovoltammetric response of unmodified PLA/CNT electrode (black) and the same electrode subjected to copper electroplating for 32 min at 6 V (red).

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Evidence of Blocking Fluorophosphate and Metal Fluoride Layers Formed During Lithiation Towards $Li_2Mn_2O_4$ in the 3V Range

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Next generation battery materials should be cheap and environmentally benign, while retaining both a high energy and power density. LMO is an interesting material as it contains only abundant materials, however, the energy density of LMO is generally limited by the relatively low capacity of 630 mAh/cm^3 and the average potential around 4V vs. Li^+/Li. The applicability and performance of LMO can be enhanced by utilizing the 3V potential range in LMO, effectively lithiating the material up to $Li_2Mn_2O_4$. Operating the material using both the 4V and 3V potential ranges, boosts the capacity to 1260 mAh/cm^3 with 630 mAh/cm^3 at 4.1V vs. Li^+/Li and an additional 630 mAh/cm^3 at 2.9V vs. Li^+/Li, leading to a net increase of 65% in energy density. This increase in energy density places the material on par with many state-of-the-art materials, such as NMC and LMNO.

There are some drawbacks. Lithiation of $Li_xMn_2O_4$ beyond x=1, leads to poor cyclability due to Jahn-Teller distortion and Mn dissolution. Improvements in the cyclability were achieved in thin films by scaling these films down to sub 100 nm thickness [1]. This was linked to suppression of the mechanical damage inflicted by Jahn-Teller distortion.

A second issue stems from electrolyte instability at the upper limit of the electrochemical window. This can be minimized by the choice of electrolyte. $LiPF_6$ in EC:DMC is a commonly used electrolyte solution due to the wide electrochemical stability window. When this electrolyte solution is used during deep discharge of LMO a peculiar decomposition reaction was observed, leading to poor cycling and rate performance. The decomposition for the given potential window (2.5V vs. Li^+/Li up to 4.25V vs. Li^+/Li) is unexpected, as the electrolyte solution is not expected to cathodically decompose above 1V vs. Li^+/Li. [2]

A comparative study of the performance of LMO utilizing both the 3V and 4V regions is conducted using different electrolyte solutions, to determine whether the reaction stems from the solvent (EC:DMC or PC) or the salt ($LiClO_4$ or $LiPF_6$) used during cycling. Based on the results, the decomposition reaction is linked to the use of the $LiPF_6$ salt and appears to be independent of the solvent used.

A reaction mechanism for this decomposition is postulated based on the formation of a blocking fluorophosphate and metal fluoride surface layer. The reaction requires the formation of a surface layer of $Li_2Mn_2O_4$ in the 3V region. XPS and ERD are combined to confirm the hypothesized mechanism.

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Assessment of electrochemically driven technologies applied to the treatment of endocrine disruptors in different aqueous matrices

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Every day different organic pollutants are being discharged into water streams and even at low concentrations can cause considerable harm to environment and human health. Currently, it is estimated that more than 87,000 compounds from natural or synthetic origin can directly affect human endocrine system [1]. These compounds are known as endocrine disruptors (EDs). The conventional physical-chemical treatments applied to treat them demonstrated low efficiencies and require long depollution times of operation. The electrochemical advanced oxidation processes (EAOPs) appeared as efficient, clean and low-cost technologies. EAOPs have been successfully used due to their simplicity combined to high performance. Little information in literature has been provided about their performance with complexes aqueous mediums. Therefore, the aim of this work is to evaluate the influence of different aqueous mediums like sulfate (SO_4^{2-}), persulfate ($S_2O_8^{2-}$) and chloride (Cl^-) in the treatment of Bisphenol A, a typical EDs. A simulated matrix that mimicked a real wastewater and tap water were also tested in order to show EAOPs viability in complexes matrices. The depurations were based on anodic oxidation with H_2O_2 eletrogerated (AO-H_2O_2) using boron-doped diamond/O_2-diffusion electrochemical cell at a current density (j) of 33.3 mA cm^{-2}. The AO-H_2O_2 process consists of *in situ* electrogeneration of physically adsorbed hydroxyl radicals ($^\bullet OH$) ($E^o(^\bullet OH/H_2O)$ = 2.80 V/SHE) from water oxidation (reaction 1), where the hydrogen peroxide (H_2O_2) is yielded by the O_2 reduction on the cathode (reaction 2).

The results highlight that EDs degradation is considerably affected by the type of water matrix. This behavior can be related to the formation of different oxidants in the medium. The kinetic constant (k_1) and dissolved organic carbon removal values increased in the following order: tap water (6.67×10^{-5} s^{-1} – R^2=0.993, 42.2%) < sulfate (1.53×10^{-4} s^{-1} R^2=0.992, 52.1%) < persulfate (2.78×10^{-4}s^{-1} – R^2=0.996, 63.7%) < chloride (5.12×10^{-4}s^{-1} – R^2=0.997, 77.2%) < simulated wastewater (1.48×10^{-3} s^{-1} – R^2=0.983, 72.8%). In the sulfate medium, the greatest contribution to EDs removal was reaction 1, where $^\bullet OH$ reacts with the contaminant leading to its overall degradation to CO_2, H_2O or partial conversion. Regarding the persulfate medium, there is the formation of sulfate radical ion ($SO_4^{\bullet-}$) through reaction 3 with the H_2O_2 electrogenerated. Sulfate radical ion has high oxidation potential ($E^o(SO_4^{\bullet-}/SO_4^{2-})$ = 2.5-3.1 V/SHE)) and longer half-life (30~40 μs) than $^\bullet OH$ [2]. Active chlorine species (Cl_2, HClO and ClO^-), obtained from Cl^- oxidation, accelerates the degradation process [3], as revealed by the acquired results.

$$BDD + H_2O \rightarrow BDD(^\bullet OH) + H^+ + e^- \quad (1)$$
$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$
$$S_2O_8^{2-} + H_2O_2 \rightarrow 2SO_4^{\bullet-} + 2^\bullet OH \quad (3)$$

The presence of inorganic ions acted as scavengers of oxidants in the tap water, justifying the poor degradation of EDs in this medium. Thus, before applying any type of treatment to water, the medium must be widely characterized with the aim of verifying what can influence the removal of the target pollutant.

Acknowledgments
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Research on *in-situ* Preparation and Characterization of Transition Metal-based Oxygen Evolution Catalysis

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Water splitting reaction involving oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) represents the core of renewable energy conversion and storage technologies. OER is generally considered to be the rate-limiting reaction due to the four-electron transfer, sluggish kinetics, and high overpotential. In the conventional mechanism of OER, the reaction includes multiple adsorbed intermediates (i.e., O–O bond formation, the rate determined step), leading to a large overpotential, while a new identified direct O_2 evolution mechanism (DOEM), which involves direct O–O coupling, has been proved to break through the limitation. Designing catalysts based on DOEM could boost the kinetics by enhancing the formation rate of O-O bonds.

Among the recently reported catalysts, transition-metal-based alloy, metal oxides and perovskite oxides show great potential. During the OER process, those electrocatalysts would go through a surface reconstruction process at high potential, especially the transition-metal-based alloy. Transition-metal based alloy is the most potential oxygen evolution catalyst due to its oxyhydroxides surface fabricated by electrochemical oxidation induced surface evolution and multi-metallic synergistic effects. Structural evolution could be achieved by electrochemically-induced continuous oxidation. It could provide more reaction sites, more active species and better water oxidation performance.

Herein, we report a homogeneous multi-metal-site oxyhydroxide electrocatalyst (consisting of Fe doped NiOOH and Cu doped NiOOH) by *in-situ* electrochemical dealloying of multi-metal-site alloy (consisting of $FeNi_3$ and NiCu alloy). The *in-situ* structural evolution process manipulates intermediate and enhances the performance of water oxidation. After dealloying, the electrochemical dealloyed catalyst exhibits a small overpotential at large current density (250 mV at 100 mA cm^{-2}), low Tafel slope (34 mV dec^{-1}), remarkably increased ECSA (8-fold larger than before), and superior durability for 200 h at 100 mA cm^{-2}. Such electrocatalyst represents one of the best performances among all reported transition-metal based electrocatalysts, even superior to benchmark RuO_2. Operando ATR FT-IR reveals that the electrochemical dealloyed electrocatalyst could manipulate the reaction path based on direct O_2 evolution mechanism (DOEM) and facilitate the formation rate of O-O bonds. The fundamental understanding would contribute to the identification and design of the active structure of oxygen evolution electrocatalysts.

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Research on Promoted Polysulfide Redox Kinetics by Graphene-Supported Carbon-Coated Ni Nanoparticles

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Although numerous efforts have been made to explore sulfur-encapsulated host materials and separator modification components (e.g., porous carbonaceous materials[1-3], metal oxides[4], and two-dimensional nanomaterials[5,6]) to physically/chemically trap sulfur species within cathodic side, they fail to facilitate intrinsically sluggish reaction kinetics of accumulated polysulfides in lithium-sulfur (Li-S) batteries. Aiming at above issue, introducing electrocatalytically active materials to cathodes or separators is regarded as an effective method to boost surface conversion kinetics of polysulfides. Nevertheless, mechanical insights of electrocatalysis are insufficient, owing to the complexity of intermediate products of the redox reactions[7]. Moreover, it should be noted that the enhanced battery performances with the introduction of electrocatalytic materials are still achieved at low sulfur mass loading (1~2 mg cm^{-2}) and excess electrolyte ($\geq$ 10 μL mg^{-1}), which is adverse to overall energy density[8-11]. Especially, it is very difficult to promote low-temperature behaviors of Li-S batteries by these reported electrocatalysts.

Herein, graphene-supported carbon-coated Ni Nanoparticles (denoted as Ni@C/graphene) was prepared by directly carbonizing the metal-organic framework/graphene oxide precursor, which was then dispersed on a commercial glass fiber membrane to form a separator with electrocatalytic activity for polysulfide conversion. *In-situ* analysis and electrochemical investigation demonstrate that the modified separator can effectively suppress shuttle effect and regulate the catalytic conversion of intercepted polysulfides, which is also confirmed by density functional theory calculation. As a result, the corresponding lithium-sulfur battery shows a high cycle stability (88% capacity retention over 100 cycles) even with a high sulfur mass loading of 8 mg cm^{-2} and lean electrolyte (6.25 μL mg^{-1}). Surprisingly, benefitting from the improved kinetics, the battery can work well at -50 ºC, which is rarely achieved by conventional Li-S batteries.

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CO2 electroreduction – challenges for different products

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The electrochemical routes are within the most promising technologies for the use of carbon dioxide (CO_2) to produce chemicals. Electrochemical CO_2 reduction not only allows for direct utilization of renewable energy but also enables the production of chemicals with neutral or even negative carbon emissions [1].

A wide range of valuable fuels and chemicals can be produced via the CO_2 reduction reaction (CO2RR) [2] from hydrocarbons [3], oxygenates [4], carbonates [5] to syngas ($CO + H_2$). The production of C1 products is possible with high selectivity and reaction rate, however more complicated compounds are requiring more electrons, are lacking high selectivity and they are facing the difficulty of the C-C bond formation. Significant work still needs to be done before CO2RR is available as a technological solution at industrial level. Moreover, each some of the possible products have different properties and are at different stages of research what makes the challenges different for each of them. For formic acid formate) synthesis from CO_2 for example, high faradaic efficiencies can be found in the literature, however stability of the catalysts in prolonged electrolysis is still unsatisfying. By the other hand, the main challenge in hydrocarbons production is selectivity

In this presentation, I will focus on the different challenges for CO2RR to different products and our recent results and strategies to tackle these challenges.

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Mesoporous Carbon Nitride based Catalyst for Efficient Water Oxidation

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Harvesting energy from sustainable sources is of immense importance to solve the current situation of the world's energy crisis. Electrochemical water oxidation is one of those sustainable ways to produce clean fuels like hydrogen. Anodic oxidation involved in the water splitting is relatively complex and its sluggish reaction pathway requires high activation. IrO_2 and RuO_2 are treated as benchmark catalysts for the water oxidation at different conditions however, their instability and high-cost limit their consistency. In this work, we report an efficient catalyst, CoS_xO_{2-x} supported on a conducting sulfur-incorporated mesoporous carbon nitride (represented as CoS_xO_{2-x}-S-MCN) synthesized by a simple and cost-effective route. For the synthesis of CoS_xO_{2-x}-S-MCN, a unique strategy is followed in which MCM-41 mesoporous silica is used as a template to create porosity and to introduce oxygen into the material. The efficiency of the CoS_xO_{2-x}-S-MCN towards the water oxidation is analyzed and compared with other reported catalysts (including IrO_2 and RuO_2) in terms of overpotential and Tafel slope values. The careful analyses/comparisons reveal that the CoS_xO_{2-x}-S-MCN exhibits ~ 2.5 times higher activity than the RuO_2 towards the electrochemical water oxidation and thus this material could be a promising alternative to replace the IrO_2 and RuO_2 based catalysts.

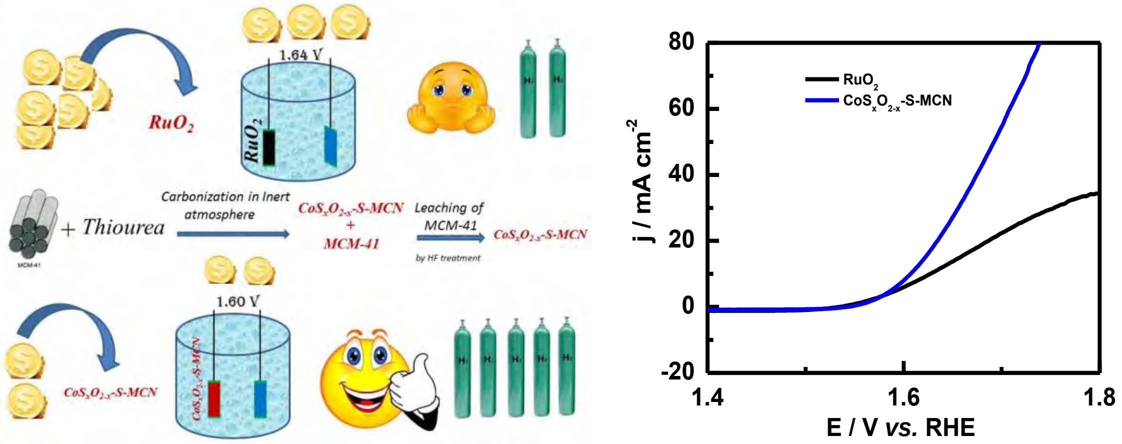

Figure: Left: Schematic representation of the higher (~ 2.5 times) water oxidation activity of CoS_xO_{2-x}-S-MCN than the RuO_2 **Right:** Linear sweep voltammetry response of RuO_2 and CoS_xO_{2-x}-S-MCN modified glassy carbon electrodes in 1.0 M KOH (scan rate: 5 mVs^{-1} and rotation rate: 1600 rpm).

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Selectivity on electrocatalytic hydrogenation using well-defined PdML electrodes: C=O versus C=C saturation.

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Selective hydrogenation is a key reaction in organic chemistry since the reducing agents available are scarce and their reaction is only potential-driven. Electrocatalytic Hydrogenation (ECH) reaction on the other hand, offers the advantages of a) being a clean procedure through electrogenerated species (electrons are the reducing agent generated in situ), b) tunable product distribution as function of the potential and c) adsorption geometry and energy can be modified by choosing the electrocatalyst.

Particularly, aliphatic ketones are readily reduced on Pt while on Pd the adsorption and reaction is largely hindered. However, the last one possesses the ability to easily hydrogenate unsaturated hydrocarbons and carbonyl groups in aromatic ketones too.

We will show the selectivity of the ECH in model molecules containing C=C and C=O groups using electrodeposited palladium monolayer on well-defined platinum surfaces. Supporting information was taken from similar electrochemical experiments employing molecules containing only one of the mentioned moieties. Comparatively, two low-index facets which showed the higher electroactivity were studied to investigate adsorption strength/orientation effects. Product distribution as function of the applied potential was monitored by *in situ* Online HPLC through a fraction collector.

However further research is needed to fully disclose the origin of the selectivity, the present result constitutes the fundamental knowledge for future scaling up in industries as important as pharmaceutical and fertilizers.

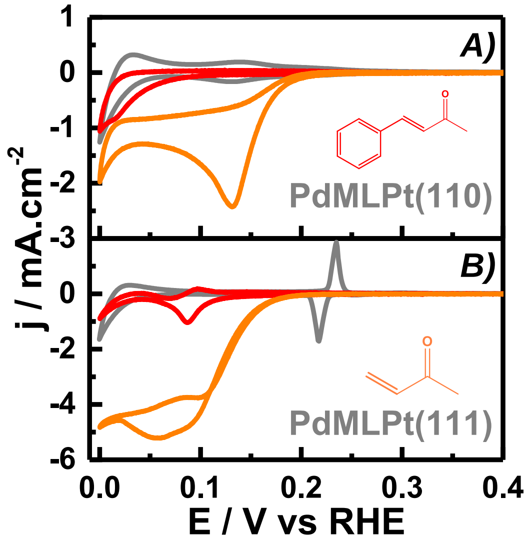

Figure 1: Cycle voltammetry of 1mM benzalcetone (red) and 10mM methyl vinyl ketone (yellow) in 0.1M sulfuric acid solution using a) PdMLPt(111) and b) PdMLPt(110) (blank CV in grey) at 50mV.s^{-1}.

Probing the Effect of Titanium Substitution on the Sodium Storage in $Na_3Ni_2BiO_6$ Honeycomb-type Structure.

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$Na_3Ni_2BiO_6$ with Honeycomb structure suffers from poor cycle stability when used as cathode material for sodium-ion batteries. Our strategy to improve the stability is to substitute Ni and Bi with the inactive Ti. Monoclinic $Na_3Ni_{2-x}Bi_{1-y}Ti_{x+y}O_6$ powders with different Ti content were successfully synthesized *via* sol-gel method and, 0.3 mol of Ti was determined as a maximum concentration to obtain a phase-pure compound. A solid-solution system of O3-$NaNi_{0.5}Ti_{0.5}O_2$ and O3-$Na_3Ni_2BiO_6$ is obtained when this critical concentration is not exceeded. The capacity of the first desodiation process at 0.1 C of $Na_3Ni_2BiO_6$ (~ 93 mAh g^{-1}) decreases at higher Ti concentration to ~ 77 mAh g^{-1} for $Na_3Ni_2Bi_{0.9}Ti_{0.1}O_6$ and ~ 78 mAh g^{-1} for $Na_3Ni_{0.9}Bi_{0.8}Ti_{0.3}O_6$, respectively. After 100 cycles, a better capacity retention is obtained for the Ti-containing structures. At 1.0 C, the stabilization effect of Ti is even more pronounced. Furthermore, a change in the multiple phase transformation was found. The O`3 phase, which forms in the first discharge process no longer exists after substitution with Ti. This leads to an improvement in the kinetics, which results in more stable cycling performance.

Keywords: Sodium-Ion-Batteries, Honeycomb-Layer, Solid-Solution, Cathode Material.

Activating $Mn(OH)_2$ as Oxygen Evolution Reaction catalyst by Electrically Interconnecting between MnO_x and Conductive Carbon

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Hydrogen is one of the promising energy carriers, which can be also utilized in the various industrial field. Among some hydrogen production technologies, water electrolysis based on anion exchange membrane is getting attention due to the availability of usage of transition metal (Co, Ni, Fe, Mn) as the catalysts. Oxygen evolution reaction (OER), which is a counterpart of hydrogen evolution reaction (HER), has a higher overpotential than HER, and it causes an increasing oxidation state of metal catalysts from +2 to +3/+4. However, the active oxidation state toward OER is limited. In the case of Mn, only Mn^{3+} is known as the active site for OER due to unstable bonding between oxygen and Mn atom. To increase the OER activity, it is important to design the MnOx with dominant Mn^{3+} by oxidizing Mn^{2+} species such as $Mn(OH)_2$ and MnO.

In this study, we investigate the role of conductive carbon of catalyst layer in maximizing active site, Mn^{3+}, in OER operating potential. We observed that $Mn(OH)_2$ oxidation peak was activated by adding conductive carbon in cyclic voltammogram, and the peak potential was dependent on the amount of conductive carbon. The relationship between the amount of carbon and activated $Mn(OH)_2$ was confirmed in terms of OER overpotential and electro-conductivity estimated by band-gap. However, carbon is generally known as undergoing corrosion in the harsh OER potential. To distinguish the carbon corrosion peak from OER oxidation peak, we conducted a rotating-ring disk electrode technique and stability test.

Electroanalytical Detection of Trace Arsenic(III) in Aqueous Media Using $AgMnO_2$ Electrode

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Arsenic is a heavy metal that exists in the Earth's crust and groundwaters. It occurs in organic and inorganic forms, with inorganic forms being more toxic than organics ones. Furthermore, inorganic As^{3+} is reported to be ca. 60−70 times more toxic than As^{5+} [1]. Prolonged exposure to arsenic in drinking water has a damaging effect on the human nervous system, respiratory system, skin, cardiovascular system, also increasing the risk of cancer. Consequently, the World Health Organization has limited the maximum level of arsenic in drinking water to 10 $\mu g\ L^{-1}$ [2]. Various analytical methods, such as atomic fluorescence spectroscopy [3] and inductively coupled plasma-mass spectrometry [4], have been employed for the detection of trace arsenic. However, these methods require expensive and robust instrumentation, and, as such, can only be used in a laboratory. Due to the mentioned shortcomings, replacement of these analytical methods by electrochemical ones, as portable, faster and cheaper, has been suggested [5].

Herein, Ag_xMnO_2 (x~0.2) of the hollandite-type structure was prepared by mixing equimolar aqueous solutions of $MnSO_4$ x H_2O and $(NH_4)_2S_2O_8$ with Ag wire added in the final solution. After 3 days of standing in the dark, the obtained powdery material was washed with absolute ethanol and distilled water several times, respectively, dried in a vacuum and finally heated for 4 h at 450 ºC.

This material was tested for As sensing in acidic media (1 M HCl) by anodic stripping voltammetry (ASV) Determination of As^{3+} on the $AgMnO_2$ electrode by ASV method proceeds in two steps: reduction of As^{3+} from the solution to As^0 and deposition of As^0 on the electrode, after which, due to the change in potential, As^0 is oxidized to As^{3+} and passes into solution.

Cyclic voltammogram (CV) of $AgMnO_2$ electrode illustrated its activity for detection of As^{3+} in 1 mM $NaAsO_2$ solution. Namely, CV of $AgMnO_2$ showed a well-defined peak at -0.6 V vs SCE corresponding to the electrooxidation of As. The possibility of using this electrode for detection of As^{3+} was tested in real samples using a sample of water from the river Drina spiked with As^{3+}. The response of $AgMnO_2$ electrode in the river sample (without any pre-treatment) was well defined with appearance of a clear peak corresponding to As^{3+}oxidation.

In this work, the $AgMnO_2$ electrode showed good activity for the detection of arsenic in acidic media and in the real sample indicating that this electrode can be a potentially good sensor for arsenic detection in aqueous media.

Acknowledgments

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Influence of Metal-Organic Framework on the Multifunctional Catalysis of Gold Nanoparticles

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The development of multifunctional catalysts becomes essential to satisfy the needs of the present world in the fields of renewable energy and sensing applications. Accordingly, researchers are very much focused on crystal engineering to develop new materials and reasonably utilize them through electrochemical technology. In this work, gold nanoparticles are wrapped by a zinc-based metal-organic formwork using a simple synthetic route. The crystalline nature of the resulting material, AuNPs-Zn-MOF is verified by powder X-ray diffraction patterns. X-ray photoelectron spectroscopy reveals the presence of Au^0 nanoparticles and their interaction with the zinc-based metal-organic formwork. Further, the AuNPs-Zn-MOF is employed for the electrochemical water splitting, electrocatalytic reduction of oxygen, and electrocatalytic oxidation of tyrosine. The electrocatalytic reduction of oxygen and the reductive water splitting processes are competitive to each other and these reactions were carefully analyzed based on the Tafel slope values. Reduction of oxygen proceeds through a two-electron process to produce hydrogen peroxide as the end product and the reductive water splitting follows the Volmer mechanism. Electrochemical oxidation of tyrosine is also catalyzed by the AuNPs-Zn-MOF. This phenomenon is advantageously used for the construction of an electrochemical sensor for the sensitive determination of tyrosine. The limit of detection and sensitivity of the fabricated sensor are found to be 3.03 µM and 0.12 $\mu A \mu M^{-1} cm^{-2}$, respectively. Thus, the AuNPs-Zn-MOF acts as a multifunctional catalyst that can be exploited further in the electrochemical energy conversion & storage and electrochemical sensing.

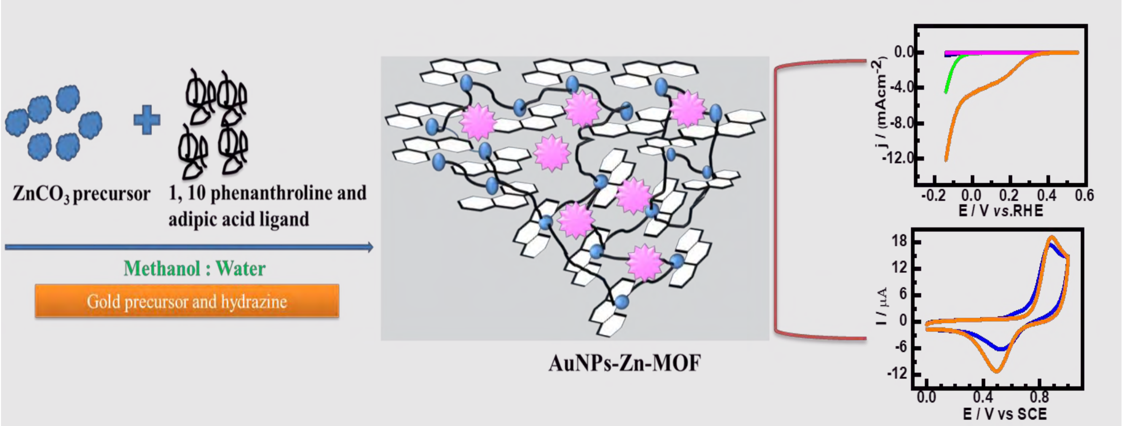

Figure: Schematic synthetic route and multifunctional catalytic activity of AuNPs-Zn-MOF.

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Self-assembled Sulfur-benzonitrile Supramolecule for Lithium Sulfur Battery

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S_8 is environmentally friendly, cheap and abundant. Its theoretical specific capacity is as high as 1675mAh g^{-1}, discharge voltage platform is 1.8V relative to Li^+/Li, and theoretical specific energy can be as high as 2600Wh kg^{-1}. S_8 is regarded as one of the ideal choice for the next generation of high energy density battery systems.According to the simulation results, the size of sulfur beam is determined, and the pore structure is reversely designed to inhibit the dissolution of polysulfide ions, and by the form of organic-inorganic compound sulfur, slow down the formation of polysulfide ions, improve the cycling performance of materials.In order to make benzonitriles with different shapes self-assemble according to a certain rule and form regular pore structure, we controlled the kinds and proportion of benzonitriles with different shapes reasonably by adjusting stirring speed, melting temperature and time; By adjusting the proportion of sulfur and benzonitrile, melting temperature and cooling rate, the in-situ SNAr and effective anchoring of sulfur and halogen are realized.

Keywords: self-assemble,Benzonitriles

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In-situ Probing of the Electrode Roughness Change during Electrodeposition in Ionic Liquids Using Electrochemical Surface Plasmon Resonance

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Ionic liquids (ILs) are promising materials for electrodeposition, because of their attractive properties such as wide electrochemical window and wide liquid temperature range. To maximize the performance of ILs for electrodeposition, studies on the interfacial structure during the electrodeposition reactions at the IL interfaces are of crucial importance. In the present study, the electrodeposition reactions at the IL|Au interface have been studied using electrochemical surface plasmon resonance (ESPR).

ESPR has shown that it can be an in-situ probe for the change in the refractive index near the IL|Au interface: both the IL side and the metal side. For the former, ESPR has been used to sensitively probe the electric double layer (EDL) structure [1,2]. ESPR revealed that the EDL structure at the IL|Au interface shows extraordinarily slow relaxation, on the order of minutes, against the potential perturbation [1,2]. This specific slow dynamics is likely to result from ionic multilayers [3-10], a well-ordered structure, spontaneously formed in the EDL of ILs. The diffusion layer of redox species at the IL|Au interface can also be probed using ESPR [11].

As for the electrodeposition, ESPR can sensitively probe the metal side of the IL|Au interface, especially the surface roughness change during the deposition/re-dissolution processes. In the present paper, we will introduce the electrodeposition of Cu and underpotential deposition (UPD) of Li on the IL|Au interface as examples [12]. For both the cases, ESPR can sensitively probe the roughness change during the multi potential cycles within which the deposition/re-dissolution of the metals repeatedly occurs. The ESPR results show the element dependence; the Cu electrodeposition and Li UPD make the Au surface flat and rough, respectively. The latter is likely caused by alloying/de-alloying of Li with Au.

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Polar Conformer Formation Determining Ionic Conductivities of Linear Carbonate Electrolytes

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The underlying nature of the ion conduction in concentrated battery electrolytes still remains elusive. An archetypal example is a long-standing puzzle why a dimethyl carbonate (DMC) solution exhibit higher ionic conductivity than other linear carbonate (LC) solutions despite the similar physicochemical properties of the LC solvents. To address this, we investigate the correlation between the conformational isomer formation and salt dissociation behavior in 0.1 M–3.0 M $LiPF_6$ DMC, ethyl methyl carbonate, and diethyl carbonate solutions using Raman spectroscopy, dielectric relaxation spectroscopy, and PFG-NMR. Importantly, we corroborate that compared to the other two LCs, DMC more readily dissociates Li-salt into free, conducting ions. The higher salt-dissociation ability of DMC was attributed to the extensive formation of polar cis-trans conformer participating in Li-ion solvation compared to non-polar cis-cis conformer, which is supported by the theoretical calculation. This study unveils the critical role of the solvent isomerism in the ion-solvation chemistry, suggesting an avenue to achieve highly conductive electrolytes for rechargeable batteries.

Active water electrolysis catalysts with Rational design of hydrogen evolution interface

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Hydrogen is an ideal energy carrier with an energy density of 140 MJ kg^{-1} and water as its final product, which is considered as an ideal candidate for the replacement of fossil fuels.[1] To date, most H_2 is produced today through nickel-catalyzed conversion of CH_4 to H_2 and CO followed by a water gas shift reaction to yield H_2 and CO_2. However, this approach is based on unsustainable fossil energy and discharges greenhouse gas. Water is an ideal source for H_2 production as it is carbon-free, plentiful and almost costless. Water electrolysis, with only H_2 and O_2 as the final product, is a highly promising route in environmental benign H_2 generation.[1-2] Although the ultimate goal is to couple hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) to an integrated efficient device for whole water electrolysis, one of the most crucial issues that must be solved is the development of highly efficient and durable catalysts for water oxidation and reduction.

Here, we build a hydrogen evolution di-anionic surface on MoS_2 material to control its catalytic activity. Specifically, sulfur anions are electronically activated by heteroatom metal doping (Pd and Ru) to acquire optimized hydrogen adsorption energy. Meanwhile, –OH anions molecularly replace S sites at the interface in a controllable manner can create a reactant benign interface. The merits of the di-anion interface with –OH anion doping are: first, –OH functional groups attracts hydronium ions and water molecules closer to the inner Helmholtz plane (IHP) through hydrogen bonding, thus contributing to a reactant friendly interface; second, –OH sites work in conjunction with adjacent metal sites (M–OH) to split water in alkaline medium, thus enormously boosts the HER catalytic behavior. We show that the HER activity of the final catalyst exhibits highest kinetic performance exceeding the existed MoS_2 based material in both acidic and alkaline environments.

Acknowledgments

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A smart transparent microscope slide for rare cell capture, single cell sensing and isolation

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The recognition of the diverse cellular behaviors, such as the different metastatic potentials of the circulating tumor cells, has triggered the need to develop single cell isolation and analysis techniques, so the information for each single cell, rather than the whole population was obtained, which could help to better understand some biological behaviors. While microelectrode array and scanning electrochemical microscopy were the common approaches to electrochemically sense a single cell of interest in a cell population, 'light activated electrochemistry', a concept developed by Gooding group, offered another potential option. Light activated electrochemistry means on an unstructured semiconducting surface, a light defined where the electroactive area is. Based on this concept, a platform has been built on crystalline silicon for single cell electrochemical sensing and even single cell isolation, by simply using a laser pointer to shine to where the target cell located. Another advantage of this platform was it was compatible to work with other rare cells enrichment techniques, so it can be applied to sense and isolate rare single cells. While it is a highly interrogated system, there are opportunities to make it more accessible for the biologist for routine applications. Inspired by the previous work, here is presented a new single cell sensing and isolation platform which builds on a transparent glass slide. It shares the same advantages as the old system but it is much more robust, simpler to fabricate and more user friendly. The first step to build this improved platform was to develop a transparent semiconducting electrode that became conducting upon exposure to visible light and were compatible with high resolution fluorescence microscopy. Subsequently, surface modification of this electrode to anchor the target cells such that they could be electrochemically sensed or release individually, has been developed. The fabrication and performance of this new single cell study platform will be illustrated in the presentation.

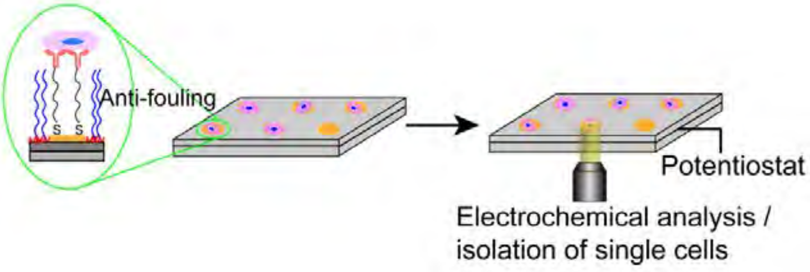

Figure 1 Cell capture, single electrochemical analysis and isolation on the smart transparent slide.

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Nitrite reduction catalyzed by silver foam: a differential electrochemical mass spectrometry study

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Metallic nanofoams are recently presenting an interest in electrocatalysis and electrochemical sensing. Application to carbon dioxide reduction [1] and glucose detection [2] have been described for silver, copper, gold and platinum foams. These materials are obtained using the dynamic hydrogen template electrodeposition. Their enhanced electrocatalytic activity is explained by the large surface, the porosity at different length scales and the existence of nanometric features such as dendrites and needles.

In this presentation, we described the use of silver foams for nitrite reduction. Although nitrite is used as food preservative, its presence in high concentrations both in human body and in the environment is dangerous. Therefore, the detection and eventually the conversion of nitrite into harmless compounds is desired. Amongst other metals, polycrystalline silver has been well characterized as catalyst for nitrite conversion [3]. It has been shown that, on the silver surface, nitrous acid (HNO_2) is converted to nitric oxide (NO) which is subsequently converted to nitrous oxide (N_2O). For the first time, silver foam is used here as electrode material for catalyzing this reaction. We have employed differential electrochemical mass spectrometry as analytical technique for the on-line detection of reaction products (Figure 1). Our main finding is that the silver foam favors the reduction of solution-phase NO (issued from the decomposition of HNO_2 at acidic pH). In the low potential range (between 0.2 to -0.1 V vs RHE) the product is N_2O. As the potential is decreasing below -0.1 V vs RHE, a change in the reaction mechanism is observed. The concentration of the solution phase NO is stable while the one of N_2O is decreasing. This is interpreted as the apparition of the reduction of HNO_2 to NO that is now subsequently converted to hydrogenated species such as NH_4^+ or NH_3OH^+ that are not detectable by DEMS.

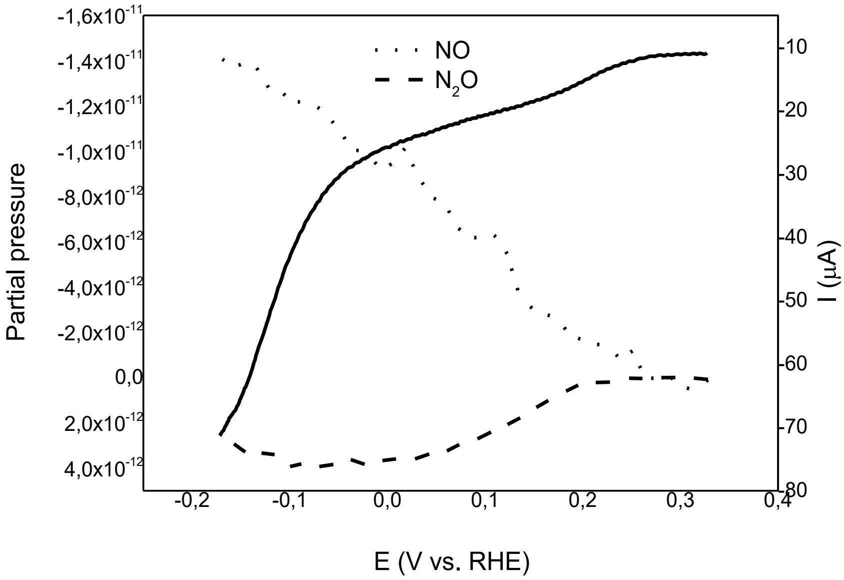

Figure 1. DEMS analysis of nitrite reduction catalyzed by **silver foam**. Black curve is the forward scan of cyclic voltammetry, dot line is the signal of m/z = 16, dash line is the signal of m/z = 46 (10 mM $NaNO_2$ containing isotope ^{15}N was used).

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Ionic Charge Transfer through the Polymer/Ceramic Electrolyte Interface determined by Electrochemical Impedance Spectroscopy

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With our increasing demand for carbon free renewable energy, the development of high energy density and safe batteries is key. Lithium (Li) metal has been identified as the ultimate negative electrode due to its particularly high gravimetric capacity (3.86 A.h.g^{-1})(*1*) and very low potential (-3.04 V *vs.* SHE, Standard Hydrogen Electrode) which are the two levers to increase the energy density in a battery. However, Li is known to form dendrites during cycling which eventually short-circuit the device and lead to a hazard issue (fire, explosion). One strategy aims then at developing all-solid-state Li batteries, which would prevent dendrite formation using solid electrolyte and increase both battery safety and cycle life.

Solid-state electrolytes fall into two major classes; polymers and inorganic ceramics. Solid polymer electrolytes (SPEs) have advantages in terms of their mechanical properties, however poor ionic conductivity (typically 10^{-5} S.cm^{-1} at room temperature, RT) hinders their application.(*2*) Conversely, ceramic electrolytes (CE) have greater thermo-stability and ionic conductivity (around 10^{-4} to 10^{-3} S.cm^{-1} at RT for NaSICON/garnet structures),(*3*) but suffer from mechanical issues (brittleness).

Composite electrolytes have therefore come to light as a possible solution comprising the mechanical properties of SPEs and the high ionic conductivity of ceramics. The addition of highly Li$^+$ conducting CE (*e.g.* NASICON, garnet…) to a polymer should reach conductivities higher than the neat polymer electrolyte. However, results are varied, including some groups that observe a decrease in the overall conductivity upon dispersion of a CE in a SPE matrix.(*4*) Investigation are thus needed to understand the reason hindering the development of composite electrolyte. A possibility for the decrease in conductivity of the composite electrolyte could be due to the high Li$^+$ charge-transfer resistance at the SPE/CE interface.(*5*)

We propose a deep characterization of the interfacial SPE/CE processes by electrochemical impedance spectroscopy. Different model layered systems based on symmetrical cells made using reversible Li (Li/SPE/Li or Li/SPE/CE/SPE/Li) or blocking stainless steel (SS) (SS/SPE/SS, SS/ SPE/CE/SPE /SS, see Figure 1) electrodes are reported to probe specifically the ionic charge transfer resistance, R_{ict}, and capacitance at the CE/SPE interface, C_i, and its impact on the effective transport properties.

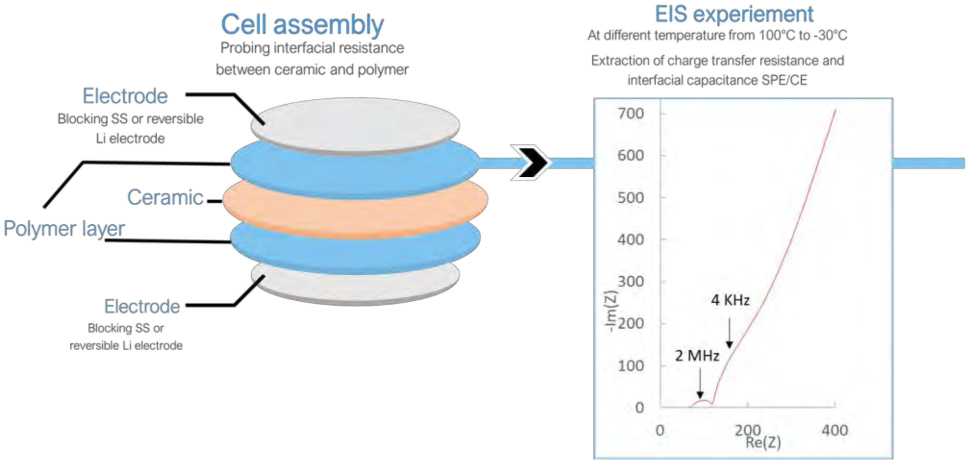

Figure 1: Experimental approach to study SPE/CE interfacial charge transfer .

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Controlled Anchoring of Metal Precursors to Prepare Fe-N/C ORR Catalyst with High-density and Highly Dispersed Active Sites

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Abstract

Oxygen reduction reaction (ORR) is an important reaction in proton exchange membrane fuel cell technology (PEMFC). Because of its excellent ORR performance, platinum is widely used in fuel cell oxygen reduction catalysis. However, platinum's high cost and insufficient resources limit its application in fuel cells. It is important to design a low-cost, high-efficiency catalyst to replace platinum. Using the cyano-modified mesoporous silica hard template (CN-SBA-15), through the anchoring of the cyano-group, a highly active, active site dispersed Fe-N/C ORR catalyst was prepared. Experimental results show that the use of cyano-functionalized templates with different loadings can improve the performance of the catalyst, which is mainly due to the high dispersion of the active sites of the prepared catalyst. Under acidic conditions, the onset potential of the catalyst with the best performance was 0.88 V vs. RHE, and the half-wave potential ($E_{1/2}$) was 0.70 V vs. RHE. At the same time, after 10,000 stability tests, only a half-wave potential attenuation of 20mV was observed, which indicates that it has excellent stability.

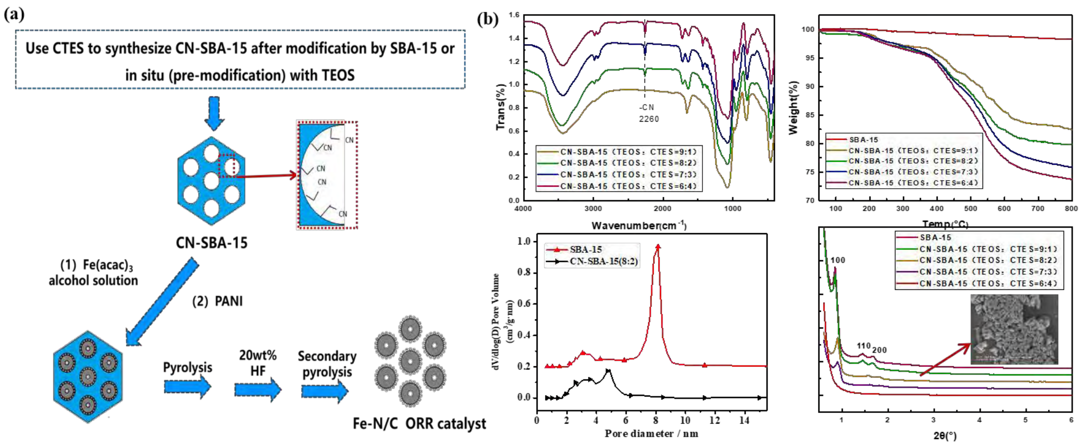

Figure 1. (a) Synthesis of CN-SBA-15 and corresponding Fe-N/C catalyst. (b) Characterizations for CN-SBA-15.

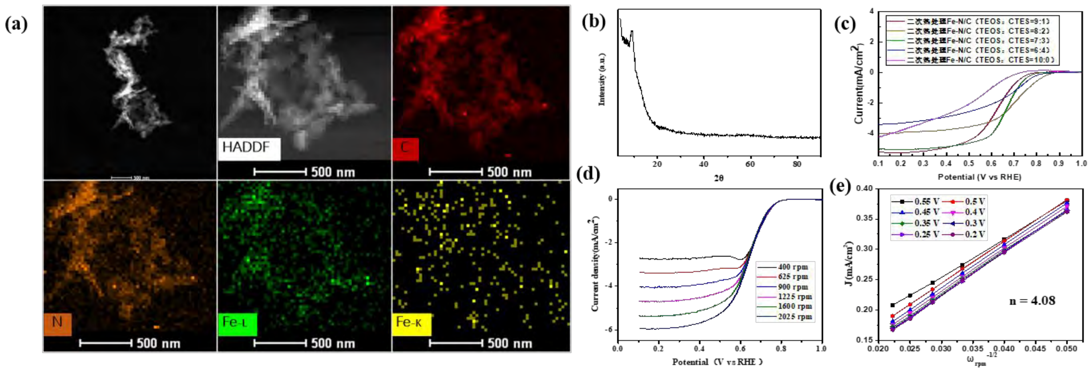

Figure 2. Characterizations for corresponding Fe-N/C catalyst.

Spinel/Lithium-Rich Manganese Oxide Hybrid Nanofibers as Cathode Materials for Rechargeable Lithium-Ion Batteries

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Lithium-rich layered oxides are promising cathode candidates to build 500 Wh kg^{-1} Li-ion batteries (LIBs) yet suffer from low initial Coulombic efficiency, rapid capacity fade, and poor rate capability. To address these obstacles, heterostructured spinel/ layered oxide ($Li_{1.15}Ni_{0.20}Mn_{0.87}O_2$) nanofibers were synthesized. The synergistic effect of nanofiber morphology and spinel/layer heterostructure enhances structure/surface stability as well as lithium diffusivity coefficient, leading to improved initial Coulombic efficiency (≈100%), cyclability (258 mAh g^{-1} after 70 cycles), and rate performance (150 mAh g^{-1} at 5C). In-situ techniques combined with first-principle calculations reveal that the spinel can stabilize the layered structure via suppressing layered structural variation as well as oxygen overoxidation and maintaining oxygen vacancy. The results would pave ways for the design of 1D heterostructure composite cathodes to develop high energy/power density LIBs.

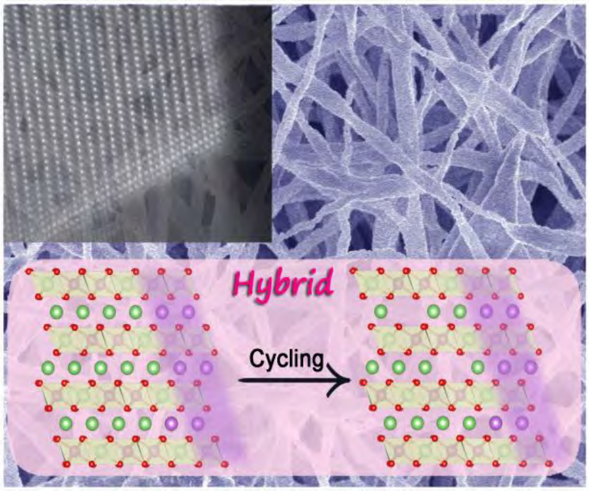

Fig.1 SEM and HAADF images of 1D spinel/layered heterostructured LLRO and illustration of stability during cycling.

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Electrochemical and DFT Study of Carbon- and Heteroatom-bridged Diarylnitroxides: a Possibility to Tune Redox-properties

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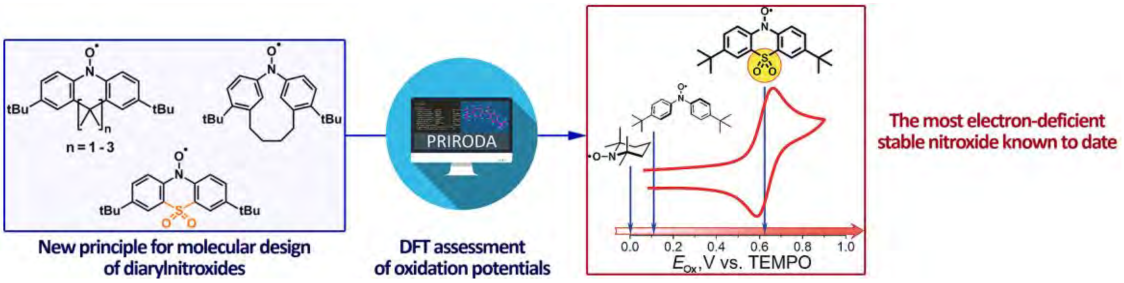
Poor ecologic situation and restricted mineral resources dictate a necessity for gradual replacement of inorganic metal-containing materials for biodegradable and recyclable organic compounds. Stable organic radicals are perspective systems to investigate since they can form several redox-states and exhibit fast electrode kinetics. Importantly, organic molecules provide wide possibilities for targeted structural modification, to obtain the properties required. In this context, diarylnitroxides seem perspective candidates. Recently we demonstrated that “twisted” donor-acceptor diarylnitroxides are smart tunable molecules capable to stabilize three redox states.[1] Herein, the opposite structural “instrument” of the molecular design is applied, i.e., partial planarization of the nitroxide molecule via insertion of carbon or heteroatomic linker connecting two phenyl rings. Prior to synthesis, the influence of such structural modification on the redox potential values was estimated, to choose the most promising structures and save material and time resources.

Quantum-chemical estimation of the oxidation potential values of novel nitroxides was performed using a combination of the “Priroda” program package at the PBE/L2 level of theory with continuum solvation model (in the form of the two-step procedure) which provides a low-cost and reliable methodology for calculation of the standard redox potentials for nitroxides in acetonitrile solution.[2] It was shown, that the introduction of a carbon-bridge (containing 1-3 methylene units between various positions of the rings) has only minor influence on the oxidation potential values (E^{Ox} are varied in the range of 0.6 – 0.75 V vs Ag/AgCl/KCl) whereas the synthetic procedure becomes more time-consuming. In contrast, insertion of the SO_2-linker between the rings gives the promising structure with the DFT-estimated oxidation potential value much more anodic than that previously measured for other nitroxides, both of aryl and alkyl type (E^{Ox} = 1.24 V vs. Ag/AgCl/KCl).

The SO_2-bridged nitroxide was synthesized and investigated using cyclic voltammetry. It was shown, that the radical is stable in solution and exhibits completely reversible oxidation at 1.33 V (vs. Ag/AgCl/KCl). This is the maximal anodic potential value achieved for reversibly oxidized nitroxides to date. One can expect that new compound might be of interest as cathodic redox material providing much higher potential gap as compared to the previously reported compounds.



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Performance of Ag-Ni-Porous Coordination Polymer as a High-quality Electrocatalyst Supporter Toward Palladium Nanoparticles

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The average temperature of the earth is being rapidly increased which can endanger human survival. It is occurred due to the high demand for fossil fuels to supply energy for citizens. One of the suggested methods to efficiently convert fuels into energy is fuel cells. The low performance and durability of available electrocatalysts toward direct ethanol fuel cell (DEFC) provide a challenging research area to either modify previous catalysts or discover new catalysts. Our recent Excremental evidence indicated that Ag-Ni porous coordination polymer (ANP) has a high-level capability to support platinum nanoparticles [1]. In the present research, the ANP was synthesized by the hydrothermal method, afterward, the palladium nanoparticles were deposited on the surface of the ANP (Pd-ANP). As a characterization test, field emission scanning electron microscopy (FE-SEM) has been taken to evaluate the morphology of the structure. To discover the performance and durability of synthesized electrocatalyst for the oxidation of ethanol, the cyclic voltammetry (CV) technique was exerted. Moreover, the Pd-ANP electrode was compared with the electrode contain palladium nanoparticles supported by carbon past electrode (Pd electrode). Additionally, a CV test was performed on the Pd-ANP electrode along 50 cycles to investigate the stability of the electrocatalyst. Electrochemical cyclic voltammetry demonstrated that forward peaks current density of Pd-ANP electrode and Pd electrode (without ANP supporter) are 5.178 $mAcm^{-2}$ (-0.246 E / V vs Ag/AgCl) and 1.782 $mAcm^{-2}$ (0.0836 E / V vs Ag/AgCl) respectively. It resulted that ANP supporter bolstered the activity of palladium nanoparticles toward electrooxidation of ethanol by almost 290%. Besides, the onset potential was decreased from the Pd electrode (-0.225 V V vs Ag/AgCl) in comparison with the Pd-ANP electrode (-0.594 V vs Ag/AgCl). The result indicates that ANP promisingly affects the kinetics of ethanol electrooxidation reactions.

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Influence of the carbon support in the electrochemical reduction of carbon dioxide using copper-based catalysts

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Carbon dioxide anthropogenic emissions are nowadays one of the most important concerns of our society to try to mitigate the Climate Change. Electrochemical catalytic reduction appears as a promising technology for recycling CO_2 to fuels or other valuable products. One of the most important challenges of this technology is the development of catalysts that can obtain high efficiencies in the reduction of carbon dioxide. In this sense, copper nanoparticles deposited on some type of carbon support are frequently used as electrocatalysts as they have demonstrated high reduction efficiencies. In this work, copper nanoparticles have been deposited using supercritical fluid deposition (SFD) technique (Figure 1) on three different carbon supports: carbon black (CB), carbon nanotubes (CNT) and reduced graphene oxide (rGO). SFD is an environmentally friendly technology that has demonstrated good results in the synthesis of nanomaterials [1,2].

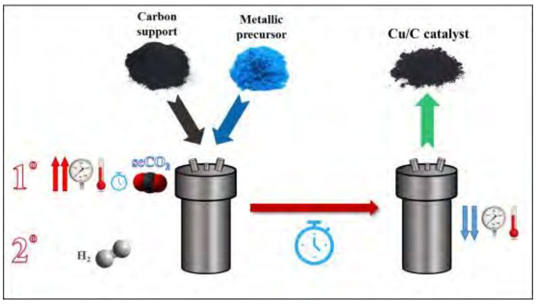

Figure 1. Scheme of the SFD technique for the deposition of copper nanoparticles

Different techniques have been analyzed to characterize the catalysts synthesized to try to understand the influence of the carbon support in the results obtained: TEM, DRX, XPS, ICP, FTIR and BET. Results show that SFD technique allows obtaining catalysts with a homogeneous copper nanoparticles distribution in the different carbon supports with deposition yields close to 90% in every case. Furthermore, most of the copper nanoparticles crystallite size is between 10 and 20 nm.

Finally, the activity of these catalysts (Cu/CB, Cu/CNT and Cu/rGO) has been determined for the electrochemical reduction of carbon dioxide in gas phase in a PEM type electrochemical cell (25 cm^2 geometric area). Every assay has been carried out in continuous mode at 0.05 SL CO_2/min of carbon dioxide circulating through the cathodic compartment of the cell. The anolyte used was a $KHCO_3$ 0.1 M aqueous solution. Temperature was fixed at 60 ºC and current density applied was 16 mA/cm^2 with four replicates for each catalyst studied.

The highest CO_2 conversion rate was obtained for the Cu/CNT catalyst. Nevertheless, products distribution was very similar in every case with CO, formic acid and methane as the main products obtained. Nevertheless, Cu/CNT and Cu/CB catalysts promote the formation of CO, whereas formic acid is the main reaction product with Cu/rGO. These results point out that the interaction between the copper nanoparticles and the carbon support plays an important role in the CO_2 electrocatalytic reduction process.

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Influence of Carbon Felt Surface Oxidation on Vanadium Redox Flow Battery Behavior

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Carbon fibers are commonly used as materials for the flow-through electrode coupled with vanadium redox pairs because of their relatively low cost, broad potential window, porosity and resistance in supporting electrolyte, i.e., acidic solution [1]. Their role is very important especially when vanadium redox flow batteries (VRFB) are considered. The key recognition of VRFB systems is the possibility to separate the energy and power values and to tailor VRFB for specific application. The energy is dependent on the size of the electrolyte storage tanks, while the power capability is determined by the size of electrochemical cells stack. This feature gives VRFB a brilliant future in energy storage systems for grid application [2].

Beside many advantages of RFB system, some side reactions (carbon corrosion and oxygen evolution on the positive side and hydrogen evolution on the negative) still lead to the significant RFB performance losses over time. Therefore, there is still a particular need to develop a material with good electrical conductivity and proper activity to improve overall RFB properties [3].

The research objective relates to broadly-defined comparison of the cost-effective carbon material treatments coupled with insightful *post-mortem* and *in-situ* physico-chemical analysis. For these studies, Rayon based graphitized carbon Sigracell® GFD 4.6 EA from SGL Carbon (Germany) was used.
In order to address the growing need of environmental friendliness using mild approaches, a new oxidation method will be adapted using neutral alkali salts such as potassium nitrate (KNO_3). Herein, a simple molten salt method is studied to prepare carbon felt electrode with novel properties. Various reaction conditions have been investigated and correlation of the activation time and temperature on VRFB behaviour will be presented.

All the electrodes were tested in three electrode cells and redox flow battery system. Moreover, physico-chemical properties such as: surface functionality, wettability and surface texture/structure have been monitored using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, elemental analysis and contact angle measurements.

It seems that application of molten salts as an activation agent can be the new route for carbon felt treatment necessary for efficient vanadium redox reactions.

Acknowledgements: Justyna Piwek would like to acknowledge the National Science Centre, Poland (project no. 2018/29/N/ST4/01055) for the financial support of the research.

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Enhancing the Activity of Alkaline Hydrogen Evolution Reaction by Lateral Electrode Structuring

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The production of solar fuels with devices based on metal-semiconductor junctions is a promising future technology of the renewable energy economy. The semiconductor part of these hybrid devices can provide an efficient absorption of solar light while the metal facilitates fast reaction kinetics. However, to fulfill these two functionalities the device requires a laterally patterned surface.

We show that lateral structuring of silicon-based electrodes with well-defined gold arrays in addition exhibits cooperative effects, i.e. strongly altered catalytic activities compared to bare gold surfaces [1]. We demonstrate this with the hydrogen evolution reaction (HER). In particular, we show that the alkaline HER rate scales with the interfacial area between the gold catalyst and the silicon oxide support [2]. A rate enhancement of an order of magnitude for the largest interfacial area is observed. We present evidence that the lateral structuring changes locally the electric field, thus giving rise to a bifunctional mechanism. The local field enhancement increases the reaction rate of alkaline HER at the interface compared to the rate at the metal bulk. The enhancement is not restricted to gold/silicon oxide boundaries. Rather, structured electrodes based on platinum catalysts exhibit also higher reaction rates than bulk Pt films. Such laterally structured silicon photoelectrodes can exhibit reaction rates for alkaline HER that are similar to the HER activity in acidic media [2].

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Design and Fabrication of Economic and Scalable all Electrodeposited $NiCo_2S_4$//Iron oxide based Asymmetric Supercapacitor

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Supercapacitors are primarily employed as energy sources for hybrid electric vehicles, back up systems, etc. owing to their high power density and life span[1]. However, meeting the energy demands require high energy densities, which can be achieved by improving the specific capacitance or widening the potential window. Besides, the quest for new anode and cathode materials have always been quintessential to improve the supercapacitor properties. In comparison to most commonly employed carbonaceous materials, metal oxides/sulfides are superior in their electrochemical performance due to the additional faradaic reactions. In this regard, the present work aims at the synthesis of $NiCo_2S_4$ as positive and iron oxide as negative electrode with nanoflower-like morphology by facile, scalable and highly economical electrodeposition route. Both the electrodes have been studied for their morphological (Fig. 1a and b), electrochemical (Fig. 1c) and structural properties. The appropriateness of $NiCo_2S_4$ [2] and iron oxide[3] as electrode materials is realized by their corresponding cyclic voltammetry (CV) and charge-discharge analyses, also exhibiting excellent cyclic stability. Thereafter, an all-electrodeposited $NiCo_2S_4$//Iron oxide asymmetric supercapacitor is fabricated with 3M KOH as the electrolyte (Fig. 1d). Thus fabricated device exhibited good energy and power density values while yielding excellent stability performance (to be discussed later). The present study shows that the electrodes synthesized by the economic electrodeposition method are highly efficient and are suitable for next-generation supercapacitor devices.

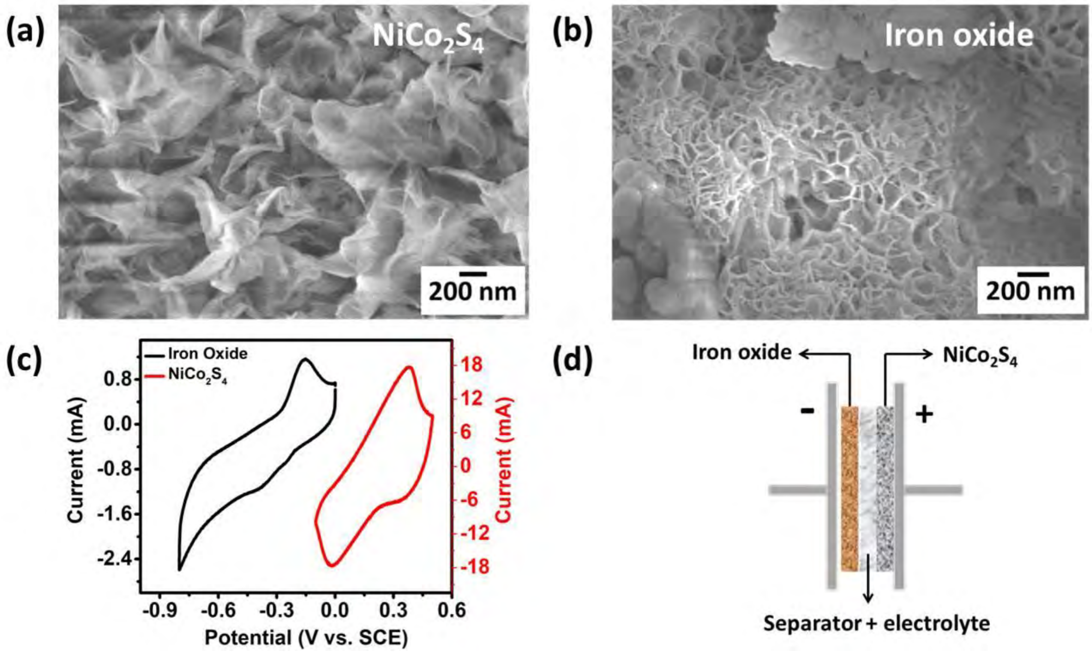

Figure 1. FESEM images of (a) $NiCo_2S_4$, (b) Iron oxide, (c) CV of $NiCo_2S_4$ and iron oxide at 20 mV s^{-1} scan rate and (d) schematic of the asymmetric supercapacitor

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Beyond energy storage limitations – long-term operation of sulfate-based electrochemical capacitors

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Lithium sulfate aqueous solution finds its application as electrolyte in electrochemical capacitors (ECs) mostly by its versatile advantages [1-2], such as:

- neutral pH,
- good electrical conductivity (for 1 mol L^{-1} Li_2SO_4 - 72 mS cm^{-1}),
- suitable ion size matching to carbon porous structure,
- reversible and satisfactory capacitive performance (95% of coulombic efficiency and 65% of energetic one when charged/discharged within the voltage range of 0-1.6 V at 0.1 A g^{-1}),
- ability to operate at high voltage (up to 1.6 V) and good long-term stability (120,000 cycles recorded during 250 days of constant operation to obtain 20% capacitance fade).

We do believe that besides many advantages, sulfate-based ECs might be further improved. Our research is focused on expanding sulfate-based ECs properties, by studying the influence of various cations (Li^+, Na^+, K^+, Rb^+ and Cs^+) on the overall electrochemical performance and ageing phenomena.

After applying constant voltage hold (*floating*) test on EC with 1 mol L^{-1} sulfate-based electrolyte, deterioration of both electrodes (namely specific surface area (SSA)) has been observed contrary to nitrate-based ECs [3]. Thus, it suggests that both electrodes participate in the ageing process. Moreover, pH tends to be a crucial factor for a long-term stability of the device. In addition, considering binding energy of cations to aromatic ring, the higher binding energy ($Li^+ >> Cs^+$), the lower SSA change. Apparently, the ion size itself does not affect textural changes of electrode after ageing test remarkably. When ions penetrate the electrode porosity, local dehydration process might occur; however, it cannot be discussed based on a full device studies and *post mortem* analysis of electrode texture, as each cation is characterized by different hydration enthalpy. Hence, three-electrode investigations are required. Large cations (Rb^+ and Cs^+) favorably lose their solvation shell, as it might be done with a low energetic cost. Small cations (Li^+ and Na^+) exhibit strong interaction with surrounding water molecules. Counter electrodes SSA fade trend resembles the following order of cations in the electrolytic solution $Li^+ < Na^+ < Rb^+ = Cs^+$. It suggests that ECs based on 1 mol L^{-1} Rb_2SO_4 and Cs_2SO_4 get aged similarly. Thus, binding energy does not play such an important role considering change of SSA of electrodes, contrary to the ions' size. It is assumed that Rb^+ and Cs^+ are too big to penetrate porosity reversibly and pore clogging effect might occur, while these cations are trapped inside micropore structure. In order to enhance system with rubidium or caesium sulfate, one need to use carbon with wider micropores (1-2 nm range) or even more developed mesoporosity. Additionally, ECs lifetime has been compared (up to C/C_0=80%) among all studied electrolytes. These results indicate that proposing a novel sulfate-based electrolyte composition, extension of operational time can be achieved (up to 650h of *floating* test).

We do correlate these findings with pH influence on SO_4^{2-} anion stability. Furthermore, time of operation of ECs with Me_2SO_4 electrolyte (where Me=Na^+, K^+, Rb^+, Cs^+) seems to be in a linear trend with cation properties, e.g., binding energy, cation diameter, hydration enthalpy. Interestingly, Li_2SO_4 does not follow this tendency at all.

Insights into sulfate-based ECs have been, herein, presented. Cation influence on the overall electrolyte performance has been described and advancement of the system has been proposed.

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Novel Approach for Lifespan Extension of Electrochemical Capacitors

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Water-based electrochemical capacitors (ECs) are nowadays intensively studied mainly due to their environmental benign and cost-effective technology. Nevertheless, their cycle-life at the higher voltages is limited because of thermodynamic water decomposition at U>1.23. Therefore, there is a particular necessity to develop long-lasting ECs operating in aqueous medium at high voltages [1].

Our previous studies allowed the capacitors failure reasons to be fully recognized in capacitive ($LiNO_3$-based) and redox (KI-based) systems. It has been proven that the oxidation of the positive electrode is one of the main problems which causes capacitance fade of aqueous medium carbon/carbon ECs. Moreover, solid-state deposit (namely Li_2CO_3) has been found for both electrodes after the ageing test [2].

Currently, our scientific scope concerns the study of capacitors with nitrate-based electrolytes operating with activated carbon electrodes. This research reports on the successful attempts of symmetric aqueous electrochemical capacitor life-span extension.

Various electrolyte concentrations were selected in order to observe its influence on capacitor operation. Long-term performance has been simulated using a constant voltage-holding test. The carbon-based electrodes after the ageing tests have been analysed and compared with pristine materials using various physicochemical techniques, such as: N_2 adsorption/desorption at 77K, XPS and elemental analysis. A modified electrochemical protocol was adapted in order to extend capacitor life-time operation. This approach allowed the properties of the negative electrode to be used. It has been proven that ECs cycle life strongly depends on the electrolyte concentration. All the systems were aged to the same relative capacitance level, i.e., C/C_0=80 %. On this basis, it has been estimated that maximally +83% of capacitor operation time extension is achieved for 0.2 mol·L^{-1} $LiNO_3$.

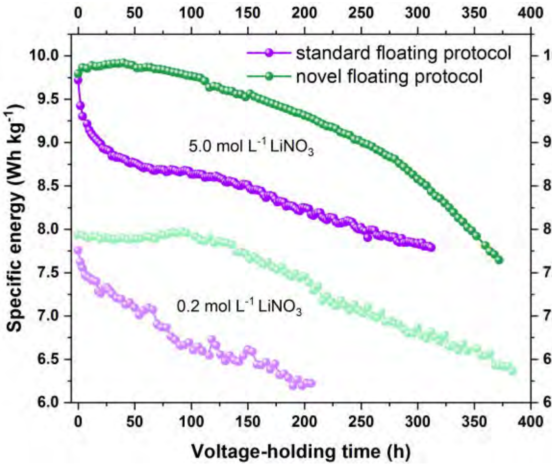

Fig. 1 Specific energy as a function of floating time for capacitors with $LiNO_3$ electrolyte at different concentration (0.2 mol·L^{-1} and 5.0 mol·L^{-1})

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Performance and stability of LSFMn+NiSDC anode in dry methane

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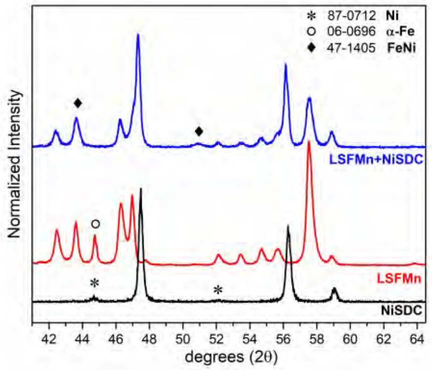
Anode deactivation over prolonged SOFC operation represents a major issue towards stable and reliable energy production from hydrocarbon-containing fuels[1][2]. In this respect, Ni-YSZ replacement with oxide-based anodes, less prone to coking, is commonly regarded as a viable solution[3]. Nevertheless, most studied oxides cannot compete with Ni-based state-of-the-art anodes in terms of conductivity and catalytic activity. A novel MIEC anodic composite based on $La_{0.6}Sr_{0.4}Fe_{0.8}Mn_{0.2}O_{3-\delta}$ (LSFMn) perovskite and $Ce_{0.85}Sm_{0.15}O_{2-\delta}$ containing 5 wt.% of Ni (NiSDC) was tested in methane fuel. In reducing conditions, LSFMn undergoes phase transformation to Ruddlesden-Popper structure, exsolving Fe^0 nanoparticles and retaining proper conductivity[4]. The small amount of Ni, well-dispersed on the SDC matrix, forms a Fe-Ni alloy with the exsolved iron from the perovskite Fig.(1). While Fe-Ni alloy activates CH_4, SDC provides enough O^{2-} ions to electrochemically oxidize any cracking products. LSGM-based electrolyte supported cells were tested in wet, dry methane and methane-based gas mixtures. Endurance cell tests at 850 °C in dry CH_4 were performed. A remarkable cell stability for over 40h was registered both in open circuit voltage and *in operando* Fig.(2). SEM and Raman Spectroscopy analyses carried out after endurance tests do not reveal any anode fouling.



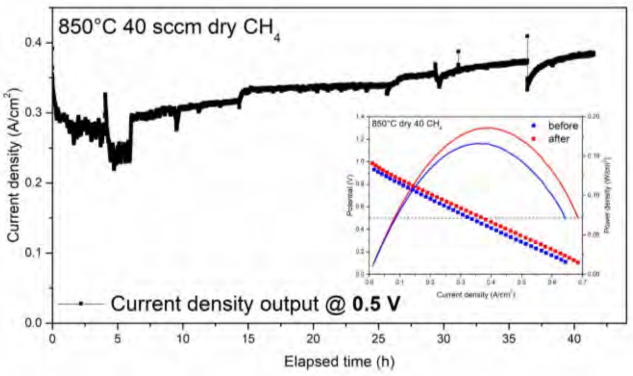


Fig. 1 – XRD patterns of reduced anodic components. From LSFMn and NiSDC co-reduction FeNi alloy formation is visible.

Fig. 2 – Endurance test in dry methane at 850 °C, current density versus time at 0.5 V. IN the inset I-V curve and power densities before and after the test are reported.

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Bio-inspired Supercapacitor an ecofriendly device for green supercapacitor

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The huge and continuously growing demand for electrochemical energy storage systems is forcing the scientific community to think about their impact on the environment. Technologies that should enable a transition to a sustainable society feature pollutants components and require a tremendous amount of energy for their production process. Supercapacitors represent a niche of the total energy storage market but are not exempt from this criticism [1,2]. Indeed, the main components of modern carbon-based Electrical Double Layer Capacitor (EDLC), such as the electrolyte solvent Acetonitrile, are known to be flammable, toxic to human health and dangerous to the environment. The binder is not immune from this kind of judgment, indeed, Polyvinylidene difluoride (PVDF) belongs to the larger family of the Per- and polyfluoroalkyl substances, also known as PFAS. It is arising the concern about their impact on the health and their capability to bio-accumulate [3,4]. The solvent needed for the processing of the electrodes, N-Methyl-2-Pyrrolidone (NMP) is also known to be toxic and irritant. The usage of this solvent represents a further drawback in terms of the device cost. Moreover, its processing requires a tremendous amount of energy for being dried [5-8]. Water processable binder and non-toxic electrolyte represent a solution to the majority of these problems [9-12]. A further step through green and sustainable supercapacitors is the exploitation of a living system to enhance the performance of EDLC devices.

Here we report the systematic study of an EDLC based on anthracite that exploits the activity of a biofilm to enhance its performance. A water processable Alginate based binder has been used and cation exchange (Sodium with Calcium) has been performed to enable its use in aqueous electrolytes [13]. Waste water was used as electrolyte. Different combinations of active carbon, binder, and electrolyte have been tested. The most performing one has been selected to build an EDLC. The growth of the biofilm has been monitored and the effect of its presence on the performance of the EDLC measured. This work highlights that sustainable and green devices have performance comparable with classical fluorinated polymer and organic electrolyte based EDLC. Furthermore. Our findings aim at paving the way towards a novel concept of “Bio-Supercapacitor” that exploits bacteria as active components for energy storage.

Acknowledgments

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Novel water processable binder for high potential Li-ion battery cathodes

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The growing energy demand in all the world is requiring for more sustainable energy production methods while the environmental and economic sustainability of these methods are of tremendous importance. Electrochemical energy storage systems are a key element for the implementation of sustainable energy systems and the transition from an economy based on fossil fuels to a low environmental impact society.
Lithium-ion batteries (LIBs) are the most well established battery technology with an exponentially growing market. However, LIBs require further improvement. In order to achieve higher energy density, the most effective strategy is to use high potential cathodes like $Li_xNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ (NMC).
Nonetheless, the environmental impact of battery production methods is of extreme importance. Today LIBs are fabricated with F-based polymers as binders, such as poly(vinylidene difluoride) (PVdF) which need N-methyl-2-pyrrolidone (NMP) as solvent/dispersant, both very toxic for humans and environment. This process also requires expensive atmosphere-controlled environment.
Here we present a novel water processable binder based on the biodegradable biopolymer Pullulan (Pu). Pu is used to process high potential NMC cathodes in ambient atmosphere. The electrochemical results of Pu/NMC cathodes are here reported and discussed and compared with those achieved with PVdF/NMC electrodes.

Acknowledgments

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Organic/inorganic hybrid electrode materials for lithium batteries

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Organic carbonyl compounds have attracted much attention in recent years because of their low cost, high abundance, flexible structural designability and environmental friendliness. However, pure small organic carbonyl materials are easily dissolved in aprotic electrolyte, leading to inferior cycling stability, low Coulombic efficiency and undesired shutting problems. We here report a dissolution-recrystallization method to prepare flexible, binder-free and free-standing hybrid film of sodium 1,4-dioxonaphthalene-2-sulfonate and multiwalled carbon nanotubes (NQS/MWNTs) as high-performance cathode for lithium batteries. The hybrid films exhibit a high initial reduction potential at 2.97 V, a high material utilization of 75%, a high capacity retention of 96% after 50 cycles at 0.2 C and good rate performance (capacity retention of 64% at 2.0 C compared with that at 0.2 C), which result from the high polarity and small size of NQS, electron withdrawing property of $-SO_3Na$ group, and three-dimensional intertwined conductive network formed by MWNTs. Moreover, the reversible redox mechanism of NQS/MWNTs during discharge/charge processes was revealed by in situ infrared spectroscopy, which indicates that the C=O groups are active sites. This study paves the way to develop well-designed organic/inorganic hybrid materials with high electrochemical performance for practical lithium battery applications in the future.

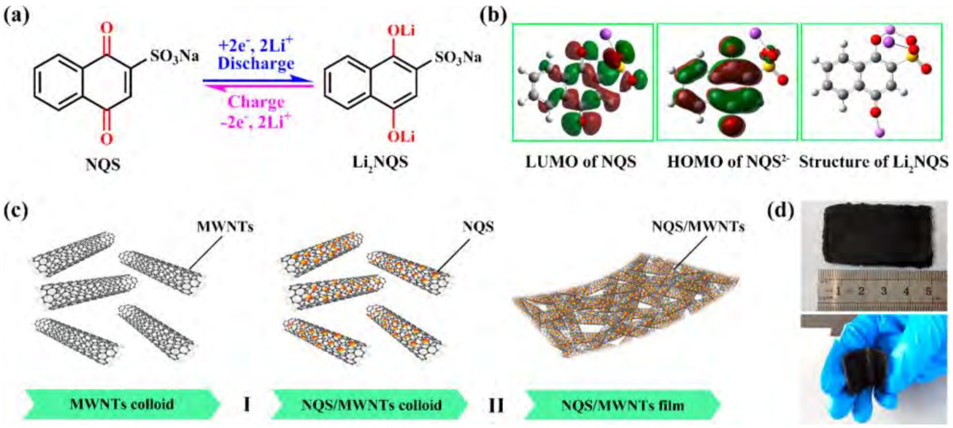

Fig. 1 (a) Structural formula and reversible electrochemical redox mechanism of NQS/Li_2NQS. (b) The lowest unoccupied molecular orbital of NQS molecule, the highest occupied molecular orbital of NQS^{2-}, and optimized structure of Li_2NQS. (c) Schematic process for preparing NQS/MWNTs hybrid film. (d) Optical photographs of NQS/MWNTs hybrid film.

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Toward First-Principles Modelling of Charged Oxide-Electrolyte Interfaces

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Oxide-electrolyte interfaces are universally present in energy storage device, nanofluidic chemical processor, drug delivery nanoparticles and containments treatment in ground water. The surface charge of all these interfaces is controlled by the pH of the electrolyte solution and this leads to the formation of the electric double layer (EDL) by deprotonation of adsorbed water molecules or protonation of the oxide surfaces. Despite of the rapid development of experimental techniques, the missing of microscopic understanding imposes a knowledge gap. In this regard, modelling and simulation of EDL can provide complementary information of the structure, dynamics and energetics of charged interfaces. Here, I will report our recent methodological progress on the atomistic modelling of dielectric properties of charged oxide-electrolyte interfaces.

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Reduction of faradaic contributions in carbon/carbon cells using a “water-in-salt” electrolyte

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Environmentally friendly aqueous alkali sulfate electrolytes with pH close to neutrality have been recently proposed for carbon/carbon supercapacitors (SCs) demonstrating enhanced voltages up to U = 1.6 V [1]. The enhanced voltages in SCs using neutral aqueous electrolytes exceeding the electrochemical stability window of water (1.23 V) is due to the increased local pH inside the porosity of negative carbon electrode due to the electrochemical reduction water producing OH^- anions and causing important di-hydrogen evolution over-potential [2]. However, it has now been established that carbon/carbon cell in 1 mol L^{-1} Li_2SO_4 keeps good state-of-health under potentiostatic floating only up to 1.5 V, beyond this voltage oxidation of positive carbon electrode occurs owing to the generation of oxygenated functionalities demonstrated by the CO and CO_2 evolution as side products [3]. Besides, reduction of water at the negative electrode generating hydrogen gas presents another challenge at high voltages contributing to pressure increase inside the cell and consequently resulting deterioration of SC performance during long-term aging/cycling [4].

In this work, we implement LiTFSI in water at two different concentrations (1 mol kg^{-1} and 21 mol kg^{-1}, pH = 6.1) in carbon/carbon supercapacitors to demonstrate the influence of electrolyte concentration on the electrochemical performance of the cell. Three-electrode cell investigations show that the hydrogen adsorption under negative polarization of carbon electrode in 21 mol kg^{-1} aqueous LiTFSI is dramatically reduced in comparison to 1 mol kg^{-1} LiTFSI. Two electrode cell data demonstrates nearly rectangular CV characteristics similar to an electrical double-layer capacitor for carbon/carbon cell in 21 mol kg^{-1} LiTFSI. Thanks to the reduced faradaic contribution at the concentration of 21 mol kg^{-1} LiTFSI owing to the negligible hydrogen adsorption and desorption at the negative carbon electrode, the cell demonstrates low self-discharge of $\Delta U = 0.178$ V. Further analyses of self-discharge data suggest the shift of activation controlled mechanisms to diffusion controlled mechanisms with the increase of concentration from 1 mol kg^{-1} LiTFSI to 21 mol kg^{-1} LiTFSI. Thermo-programmed desorption performed on the carbon electrodes in 21 mol kg^{-1} LiTFSI suggest a sudden mass loss at around 450 °C owing to the decomposition of LiTFSI trapped inside the electrode porosity.

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Effects of Oxygen Contamination on the Electrochemical Carbon Dioxide Reduction Reaction Catalyzed by Cu Nanoparticles

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The electrochemical carbon dioxide reduction reaction (CRR) in aqueous media is a promising approach to closing the carbon cycle. After Hori *et al.* reported that Cu metal electrodes selectively reduced CO_2 to various organics [CO, CH_4, C_2H_4, EtOH, Pr^nOH][1], numerous studies have described Cu-based electrocatalysts for CRR. The electrocatalytic activity of Cu-based catalysts has been generally evaluated using synthetic pure CO_2 gas (> 99.99%). However, low-purity CO_2 emitted from factories will become the substrate in the real application of CRR, and thus, a certain amount of impurities are inevitably contaminated. Among various contaminations, oxygen contamination in CO_2 gas would become a significant problem because oxygen is more easily reduced than CO_2. However, there is no systematic study on the effect of contaminant oxygen on the CRR catalyzed by Cu-based catalysts.

Herein, we investigated the effect of oxygen contamination on CRR on a gas diffusion electrode carrying copper nanoparticles (Fig.1). The CO_2 gases containing oxygen (0%, 1%, 2%, 3%, 4% and 5 %) were used as the model substrate. CRR activity was evaluated under a potentiostatic condition (-3.0 V vs. Ag/AgCl without IR collection). In the absence of oxygen (i.e., pure CO_2 gas), the total faradaic efficiencies(FEs) of hydrocarbons (methane and ethylene) reached up to 24 %. Then, the total FE of hydrocarbons decreased to 3.6 % by the addition of 1 vol% oxygen in pure CO_2 gas. Interestingly, the production of hydrocarbons was more largely suppressed than CO or HCOOH production in the presence of oxygen contamination. In the poster presentation, we will discuss the detailed mechanism for the suppression of the evolution of hydrocarbons in the presence of oxygen.

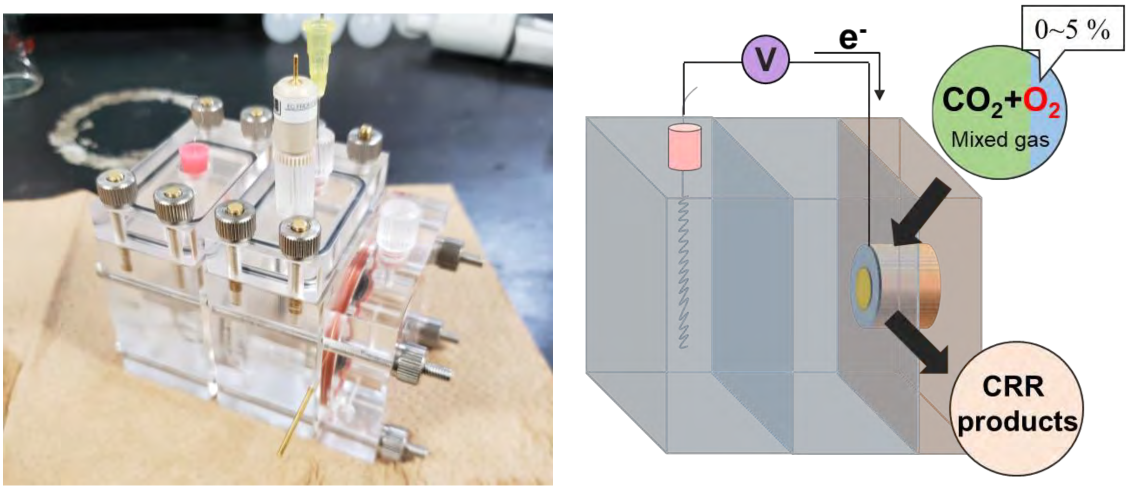

Fig. 1 (left)The electrochemical cell for gas diffusion electrodes. (right) Schematic illustration of experimental setup.

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Pullulan as green components for supercapacitors

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The increasing market of storage systems such as supercapacitors and batteries is leading the research towards new sustainable materials, to reduce their environmental and economic impact [1]. The utilization of water-processable, biodegradable electrodes and separators is a viable approach to develop green and easy-to-dispose devices. Natural polymers processed by aqueous solutions are a very promising alternative to fluorinated polymers like polyvinylidene difluoride that also requires the use of the toxic N-Methyl-2-pyrrolidone solvent [2,3]. Electrospinning is an emerging technology for the preparation of non-woven free-standing fiber mats to be used as electrode materials and separators in supercapacitors. Enabling the utilization of novel bio-derived polymer as primer giving also the possibility to use environmentally friendly solvents.

Here, we report about a systematic study on electrospun no-woven separators for high voltage carbon-based electrical double layer supercapacitors (EDLCs). Two natural polymer-based electrospun separators have been tested in three different organic electrolytes. In particular, for all the combinations of separator/electrolyte, it has been studied the stability and the resistive contribution.at different operating temperature trough Electrochemical Impedance Spectroscopy (EIS). Natural polymer-based water processable binders have been studied too. Out study demonstrates for the first time that pullulan can be used to produce high mass loading electrodes (> 10 mg cm^{-2}) at low binder content (10%) for ionic-liquid based EDLCs. 3.2 V- Pullulan-ionic liquid EDLCs featured specific energy and power of 7.2 Wh kg^{-1} and 3.7 kW kg^{-1} along with good cycling stability over 5000 cycles.

Acknowledgments

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Operando Identification of the Defect Structural Reconsitution during Oxygen Evolution Reaction

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The exact role of defect structure on transition-metal compound for electrocatalytic oxygen evolution reaction (OER) is a very dynamic process and unclear. Despite of the poor intrinsic activity of pure Co_3O_4, various modification strategies have been developed to enhance the OER activity, such as defect engineering with introduction of oxygen vacancy (V_O). However, the role of defect in catalyst materials has not yet been fully identified. V_O-rich Co_3O_4 has been widely reported as advanced OER electrocatalysts, the mechanism of which was preliminarily attributed to the enhanced electronic conductivity and more low-valence Co (Co^{2+}) formed. In addition, the chemical environment of defective Co_3O_4 is more dynamically changeable during electrocatalysis with applied potential. Studying the structure-activity relationship of defective electrocatalysts under *operando* conditions is crucial for understanding their intrinsic reaction mechanism and dynamic behavior of defect sites. Co_3O_4 with rich V_O has been reported to efficiently catalyze OER. We constructed pure spinel Co_3O_4 (as model catalyst) and V_O-rich Co_3O_4 to study the defect mechanism and investigate the dynamic behavior of defect sites during the electrocatalytic OER process by various *operando* characterizations. *Operando* EIS and CV implied that the V_O could facilitate the pre-oxidation of the low-valence Co (Co^{2+}, part of which was induced by the V_O to balance the charge) at relatively lower applied potential. This observation confirmed that the V_O could initialize the surface reconstruction of V_O-Co_3O_4 prior to march during OER process. The *quasi-operando* XPS and *operando* XAFS results further demonstrated the oxygen vacancies were filled with OH^* firstly for V_O-Co_3O_4 and facilitated pre-oxidation of low-valence Co, and promoted reconstruction/deprotonation of intermediate Co-O-OH. This result provides insight into the defect mechanism in Co_3O_4 for OER in a dynamic way by observing the surface dynamic evolution process of defective electrocatalysts and identifying the real active sites during the electrocatalysis process. The current finding would motivate the community to focus more on the dynamic behavior of defect electrocatalysts.

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$FeCo_2O_4$/CNF Prepared by Electrospinning as Bifunctional Oxygen Electrode for Alkaline Metal-Air Battery Applications

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A new way to produce and store electrical energy is necessary to address future energy demands and reduce polluting emissions. Rechargeable alkaline metal–air batteries are envisaged as commercially viable energy storage devices due to their high theoretical energy densities respect to lithium-ion batteries. However, they do not still offer adequate practical energy density and life cycle due to critical problems arising from the positive electrode, such as slow kinetics of the oxygen reduction (ORR) and oxygen evolution (OER) reactions. In the last few years, research was focused on the development of highly efficient oxygen reduction/evolution catalysts based on transition metals, such as Co, Fe, Mn, La, etc, in the form of mixed oxides (perovskites, spinels, etc.), or advanced carbon materials. Co-based catalysts have been thoroughly investigated for the ORR/OER, and, usually, Co_3O_4 is the most employed formulation. However, the electrical conductivity of bare Co_3O_4 is not appropriate for the application in most of these devices. Other transition metals (Ni, Fe, Mn, etc.) can partially replace Co atoms in the Co_3O_4 spinel structure, improving its electronic conductivity while promoting oxygen evolution. Another approach is to combine these oxides with carbon nanostructures, in particular graphitic ones, in order to maintain suitable stability under cycling operation. Recently, carbon nanofibers (CNF) synthesized by electrospinning, modified with a spinel Co_3O_4 [1] or a combination of cobalt oxide and metallic cobalt (CoO-Co/CNF) [2] or loaded with Nickel-cobaltite [3], were investigated in our laboratories as bifunctional air electrodes showing good reversibility and stability. In this work, Fe partially replaces Co atoms in the Co_3O_4 spinel structure, leading to a $FeCo_2O_4$/CNF, by using the same electrospinning preparation procedure previously reported. The $FeCo_2O_4$/CNF catalyst is physico-chemically studied in terms of structure, morphology and surface properties; these features are correlated to the electrochemical behavior for the oxygen reduction (ORR) and oxygen evolution (OER) reactions in comparison with previously developed Co_3O_4/CNF [1] and state-of-the-art materials. An outstanding onset potential towards the OER of 1.40 V vs. RHE is observed, which is 140 and 250 mV lower compared to the pure spinel (Co_3O_4/CNF) and Pt/Vulcan, respectively. A remarkable reversibility ($\Delta E = E_{OER} - E_{ORR}$) value of 495 mV is obtained, due to a good activity also for the ORR. To assess the stability of the catalysts for rechargeable alkaline metal-air batteries, cycling operation and chronopotentiometric experiments are carried out, showing promising results.

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Aqueous Electrochemical Reduction of Dinitrogen to Ammonia by Metal-doped Covalent Triazine Frameworks

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Ammonia is an important raw material of various chemical products, including resins and fertilizers. The present industrial technology for ammonia synthesis, Haber-bosch process, needs a grand scale because it requires high pressures and temperature. Recently, an aqueous electrochemical reduction of dinitrogen to ammonia has attracted much attention as an on-demand technology for ammonia synthesis because it can operate under ambient conditions. An active electrocatalyst to split the stable N-N bonds in dinitrogen is required for efficient electrochemical devices. Choi *et al.* theoretically predicted that single early-transition-metal (ETM) atoms (such as Mo, V, and Ti) doped into *sp2* carbons serve as the active catalytic sites for dinitrogen reduction reaction due to the efficient π back-donation to N-N bonds. 1) However, single ETM atoms easily aggregate to oxides or hydroxides in aqueous solutions. Recently, our group has demonstrated that covalent triazine frameworks (CTFs) could support a wide variety of metals via coordination bonds. Interestingly, the metal-doped CTFs (M-CTFs) exhibited electrocatalytic functions depending on the metal species2)-4). Therefore, we expect that the CTFs can stably immobilize single ETMs and catalyze dinitrogen reduction reaction.

In the present work, we attempt to synthesize efficient electrocatalysts composed of M-CTFs for the dinitrogen reduction reaction. First, we selected effective metal active centers using density functional calculations (DFT). Then, we evaluated the dinitrogen reduction activity of the synthesized M-CTFs using gas diffusion electrodes (GDEs), as shown in Figure 1. In the poster, we will present the detailed results of DFT and electrochemical dinitrogen reduction activity of M-CTFs.

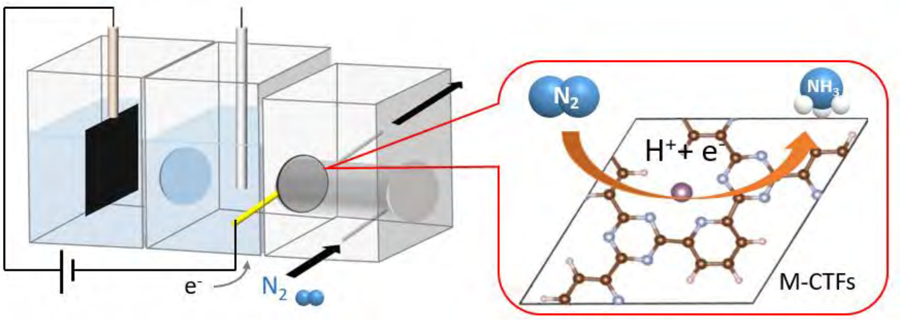

Fig.1 Schematic illustration of the electrochemical setup for the GDE carrying M-CTFs.

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Pyrrolidinium-based polymer electrolytes for supercapacitor applications

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Supercapacitors are electrochemical energy storage devices that achieve high power density and fast charge-discharge rates. In a traditional supercapacitor, an ion-permeable and electrically insulating separator film is sandwiched between two electrodes flooded with a liquid electrolyte. Since liquid electrolyte leakage is a severe issue, especially when the material is environmentally hazardous, efforts are focused on replace the liquid electrolytes with solid electrolytes. The polymer electrolytes are ideal candidates for next generation solid supercapacitors, which are not only safer, but also offer high performance, light weight, and flexible forms [1].

A method of polymerization and chemical modification was applied for synthesis of a series of novel pyrrolidinium - containing homo- or copolymers and their turning into polymeric ionic electrolyte. The polymer electrolyte was impregnated the active layer of the activated carbon supercapacitor electrodes and the resulting thin polymer electrolyte layers on both electrode surfaces are integrated into a single thin layer minimizing interfacial resistance. The electrochemical characteristic of the assembled supercapacitor cells and also of systems consisting of carbon electrode and mixtures of ionic liquid and PIL (with varying composition) were evaluated using galvanostatic charge/discharge tests and cycling voltammetry. The effect of polymer composition and operation temperature on the supercapacitor performances was also studied.

It has been found that the use of PIL in supercapacitors leads to stabilization of its capacity, as well as to increased efficiency of the charge-discharge process. Further studies are needed to improve their electrochemical characteristics.

Acknowledgments: *This work was financially supported by the Bulgarian National Science Fund through KP-06-OPR 04/5 project and partially by the National Roadmap for Research Infrastructure 2017-2023 "Energy storage and hydrogen energetics (ESHER)", approved by DCM # 354/29.08.2017 and granted by the Ministry of Education and Science of Republic Bulgaria.*

Keywords*: polymer electrolyte, supercapacitor, electrochemical tests, biogenic activated carbon*

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Influence of Ionomer Content on Oxygen Transport Resistance and Performance in PEMFC

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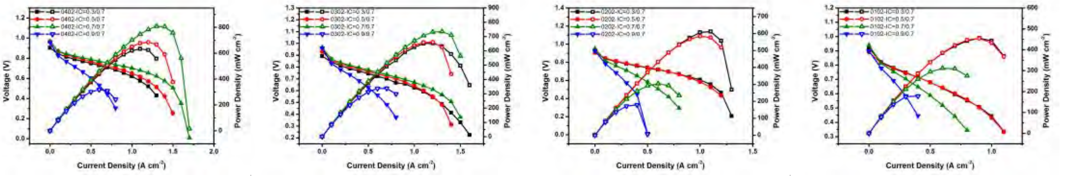
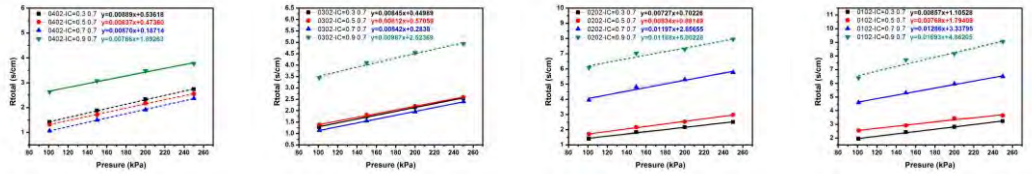
Proton exchange membrane fuel cell (PEMFC) is considered to be an ideal clean energy technology. However, its commercial application is still limited by cost and performance under high current densities. Previous research has shown that the performance loss of the MEA with low Pt loading mainly comes from the oxygen transport resistance at the cathode reaction site. Despite the ionomer content in catalyst layer has been accepted as one of the impact factors, few research focused on the in-situ measurements of oxygen transport resistance and further analysis. In this study, different ionomer content cathode catalyst layers with I/C varying from 0.3 to 0.9 were made. Oxygen transport resistance was characterized through limiting current density, the total oxygen transport resistance, Fick diffusion resistance, and local oxygen transport resistance were all calculated. Results show that ionomer content has strong influence on both Fick diffusion resistance and local transport resistance. Reasons of the influence can be attributed to the change of pore structure and the increase in thickness of ultra-thin ionomer film at the surface of platinum particles. Based on the results, ionomer content in low Pt loading catalyst layers should be minimized to reduce oxygen transport resistance and improve the performance at high current densities.



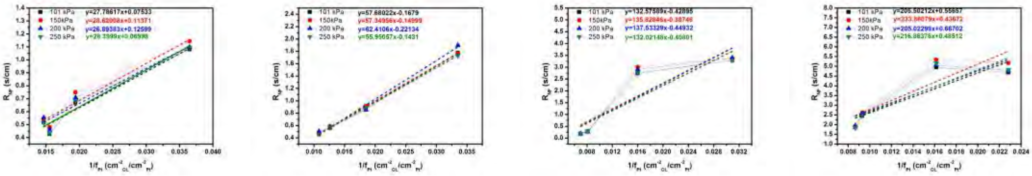
(a) (b) (c) (d)

Figure 1. Polarization curves and power density curves of CCMs with cathode Pt loading as (a) 0.4 mg cm^{-2}, (b) 0.3 mg cm^{-2}, (c) 0.2 mg cm^{-2}, (d) 0.1 mg cm^{-2}, with ionomer content as 0.3, 0.5, 0.7, 0.9, at 65℃, 100% RH, H_2/Air with constant flow rates as 150/1500 ml min^{-1}.



(a) (b) (c) (d)

Figure 2. Plot of R_{total} vs. *Pressure* of CCMs with various ionomer content and Pt loading. The slope was obtained from a linear fit giving the value of R_F.



(a) (b) (c) (d)

Figure 3. Plot of R_{total} vs. $1/f_{Pt}$ of CCMs with various Pt loading and pressure under different ionomer content (a) I/C=0.3, (b) I/C=0.5, (c) I/C=0.5, (d) I/C=0.7. The slope was obtained from a linear fit giving the value of $R^{Pt}_{,O2}$.

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Influence of DNA surface density on a sensitivity of tetracycline measurements

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Biosensors are small devices employing biochemical molecular recognition properties as the basis for a selective analysis. Such devices consist of a biological recognition element with a physical transducer [1]. In recent years, biosensors became popular in monitoring biological and synthetic processes in the field of food analysis and in the area of human monitoring and diagnostics [2]. DNA biosensors are based on nucleic acid recognition layers which can be easily synthetize and unlike enzyme or antibodies biosensors, DNA biosensors can be regenerated for multiple uses [3].

In this project we present a study on detection limit of tetracycline, widely used in animal breeding [4], using a DNA biosensor with different surface densities of DNA probe. In order to attach to the gold surface, DNA chain has to be modified with a short thiol. Thiolated DNA is capable of forming self-assembled monolayers onto gold transducers by covalent linkage to the surface via functional alkanethiol-based monolayers [5]. We used electrochemical techniques including impedance spectroscopy to characterize layer of biological probe on the electrode surface. During the interaction between DNA aptamer on the surface and tetracycline, the charge transfer resistance between the solution and the electrode surface changes, which allows to determine tetracycline concertation in solution. Surface plasmon resonance spectroscopy was used for real time observation of antibiotics interactions and determination of layers thickness.

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Dynamic behavior analysis of ion transport through a bilayer lipid membrane by an electrochemical method combined with fluorometry

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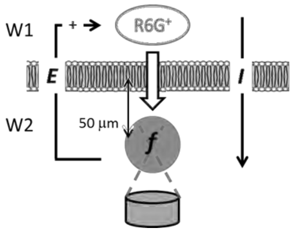
Analyzing ion transport through an artificial bilayer lipid membranes (BLMs) is essential for understanding biomembrane phenomena (such as neurotransmission and respiration) and delivery of ionic drugs into a cell.

The mechanism of ion transport through a biomembrane was conventionally studied by electrochemical methods such as the patch clamp method[1] and voltammetry[2,3], which provide a dynamic and highly sensitive analysis of ion transport through membranes. In the electrochemical methods, it is not easy to identify the transported ion from the transmembrane current. For example, a cation transfers through a membrane from an aqueous phase with more positive potential to another aqueous phase with less positive potential, yielding a positive current in the electrochemical measurement. However, the transport of an anion through the membrane in the opposite direction also gives a similar positive current. Besides, electrochemical methods cannot detect the coupled transports of cations and anions or the anti-transports of two ionic species with the same charge as electric current.



E: the applied potential
I: the transmembrane current
f: fluorescent intensity

Fig. 1 Schematic of the experimental set-up.

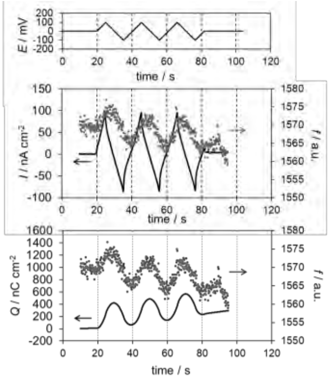


Fig. 2 Transmembrane current, *I*, Transmembrane charge, *Q*, and fluorescent intensity, *f*, recorded synchronously with membrane potential, *E*.

The combination of the electrochemical method with fluorometry solves the disadvantage of the electrochemical method, e.g. difficulty in characterization of the ion transported through a BLM in the presence of other ions. In the present work, the ion transport through a BLM caused by both a fluorescent cation (rhodamine 6G$^+$, R6G$^+$) and a relatively hydrophobic anion (BF_4^-) was examined by utilizing the electrochemical method combined with fluorometry, in which the transmembrane current and fluorescent intensity in the local area close to the planar BLM were simultaneously measured as a function of the applied membrane potential[4].

Fig. 2 indicates *I* and *f*, which were recorded simultaneously during scanning *E* between −100 mV and 100 mV. In the presence of R6G$^+$, the amplitude of *f* appeared synchronously with *E*, and the amplitude of *I* also increased. To compare *I* to *f* more precisely, we converted *I* to the total charge of the transported ions, *Q*, by integrating *I*. The positive *Q* increased for positive *E* of W1 as compared with W2. The results mean either R6G$^+$ transport from W1 to W2 or BF_4^- transport in the opposite direction. *f* increased with the increase in positive *Q*, and then we characterized the increases in *Q* and *f* as the R6G$^+$ transport from W1 to W2 through the BLM.

Using this method, the influence of a coexisting anion on R6G$^+$ transport through a BLM was examined and it was found that the R6G$^+$ transport was facilitated by the addition of hydrophilic anions such as BF_4^-.

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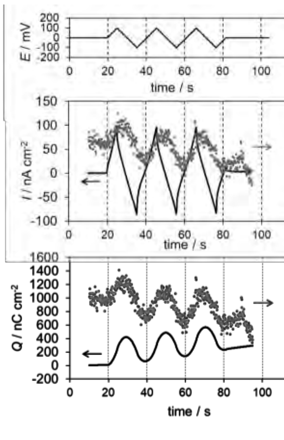

Three-Dimensional Networks of S-Doped Fe/N/C with Hierarchical Porosity for Efficient Oxygen Reduction

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Reasonable design and synthesis of Fe/N/C based catalysts is one of the most promising way for developing precious metal-free oxygen reduction reaction (ORR) catalysts. Here, nitrogen and sulfur doped catalyst were synthesized (Fe-N-C-S) using ferric chloride hexahydrate as Fe source, Potassium thiocynate as Sulfur source and Polyvinylpyrrolidone (PVP) as Carbon and nitrogen source. The obtained catalyst shows three dimensional macroporous structure. This method has the advantage of using Potassium thiocynate as Sulfur source during the synthesis process, which resulted in high doping of sulfur (about 5.4 %). The optimal catalyst shows high ORR activity with a half wave potential of 0.880 V, vs RHE and limiting current density of 6.5 mA cm^{-2}. The synthesized Fe-N-C-S catalyst showed stability in both acidic and basic media.

Keywords: oxygen reduction reaction, three dimensional macroporous structure, zinc-air batteries

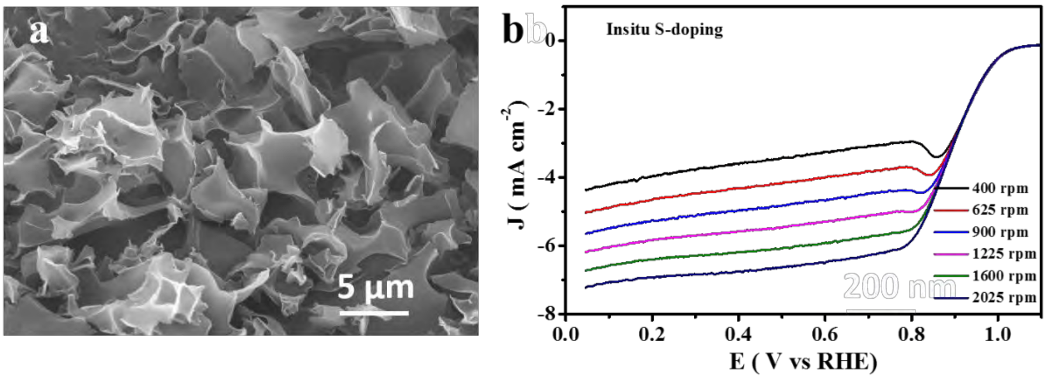

Figure 1. (a) SEM for Fe-N-C-S (b) LSV at different rpm for Fe-N-C-S

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Facile Electrochemical Synthesis of Copper-Cobalt Oxide Nanostructures for Efficient Water Splitting

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Copper-cobalt oxides, $CuCo_2O_4$ have attracted a great deal of research interests in a wide range of applications such as oxygen evolution reaction, oxygen reduction reaction, hydrogen evolution reaction, alcohols oxidation, H_2O_2 decomposition, urea oxidation, and energy storage. These are cost-effective and low-toxic and their controllable composition, electronic structure, valence states or redox characteristics, morphology, and high catalytic property have made them suitable as universal catalysts. However, their low intrinsic electrical conductivity still overshadows their practical application to some degree. In addition, the conventional preparation procedures of copper-cobalt oxide result in relatively low catalytic activity or large OER overpotential for catalytic reactions. In the present report, nanostructured copper–cobalt oxide ($Cu_xCo_{3-x}O_4$, CCO) electrodes are grown directly on conducting substrates via electrochemical deposition; then, various factors (e.g., oxygen vacancies, electrochemically active surface area, and electrical conductivity) affecting their electrocatalytic activity for overall water splitting are studied. The observed oxygen evolution reactions (OERs) performance decreases when increasing the annealing temperature due to the nanostructure deformation and agglomeration and the decreased number of oxygen vacancies, electrochemically active surface area, and electrical conductivity.

The configuration and electrochemical performance of Li-Na hybrid batteries

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Due to the low cost, wide distribution, low electrochemical potential (-2.73 V vs. standard hydrogen electrode) and high theoretical specific capacity (1166 mA h g^{-1}), Na metal anode attracts attentions in the applications of high-energy and low-cost energy storage systems. However, Na has high reactivity with the electrolyte, leading to the formation of a solid electrolyte interface (SEI) layer between Na and electrolyte. During the repeated Na plating/stripping, Na metal anode shows uneven deposition and a huge volume change, rendering the breaking and re-forming of SEI. The consumed Na metal anode and electrolyte lead to low coulombic efficiency (CE) and battery failure. Meanwhile, uneven Na plating results in the growth of dendritic Na, leading to internal short circuit and safety concerns. Thus, it is important to restrict the dendritic growth and improve the CE of Na metal anode.

The electrochemical performance and mechanism of Li and Na metal anode in ether-based electrolyte were investigated. Due to its lower reduction potential, Li^+ cannot be reduced and forms Li^+ electrostatic shield layer to guide Na plating. We also observed the dynamic plating process via in-situ optical microscope that proves the unique Na plating pattern. In addition, Na metal anode shows higher reversibility with an average CE of 99.2% and faster plating kinetics than Li metal anode. We utilized density functional theory calculation to understand the solvation/desolvation of metal-ions, and proved the fast desolvation kinetics of Na^+. Moreover, $LiFePO_4$ cathode was used to construct an advantage-complementary Li-Na hybrid battery system (LNHB). During the discharge/charge processes, Li^+ and Na^+ play roles in insertion/extraction into/from the cathode and stripping/plating of the anode, respectively. The LNHB with the high reversibility, stability and fast kinetics of Na metal anode shows low voltage hysteresis and long-term cycling.

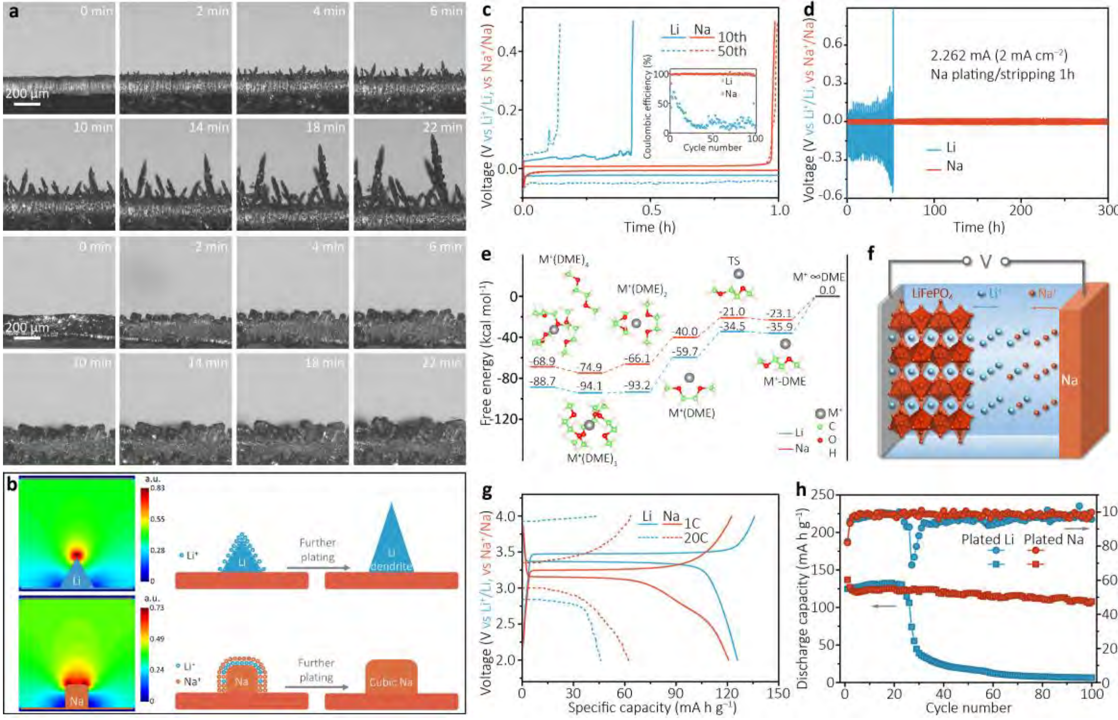

Fig. 1 (a) In situ optical observations of Li/Na plating. (b) The simulated electric field intensity distribution and schematic illustration of Li/Na plating patterns. Voltage profiles of (c) Li/Na-Cu batteries and (d) Li/Na symmetric batteries. (e) Free energy profiles of Li^+/Na^+ solvation process. (f) The configuration of LNHB. (g) Rate performance and (h) cycling performance of LNHB.

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Biowaste derived M-N-C/S catalyst use as an active electro catalyst for Zn-air battery

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In this work, we design an improved strategy to create an ORR catalyst by using sustainable bio waste materials (peanut shells) as source of carbon, nitrogen and sulphur. This method is proceeded by; chemical activation with KOH, intrinsically doped with nitrogen as well as sulphur, while extrinsically doped with iron in order to get a catalyst with enhanced ORR catalytic performance. The SEM images revealed 3D hierarchically graphitic micro and mesoporous structure with high surface area of about 1020.3597 m²/g. The EDX, mapping and XPS confirms the formation of Fe-N-C/S catalyst. The synthesized Fe-N-C /S displays excellent ORR activity with a half wave potential of (0.87 V versus RHE), limiting current density 5.31 mA cm^{-2} and onset potential of 1.13 V in 0.1 M KOH solution. This work will be surely helpful for the design and synthesis of biomass resource as facile route to change renewable bio waste materials to a valuable electro catalyst for Zn-air batteries.

Key words: biowaste, peanut shells, oxygen reduction reaction and Sulphur.

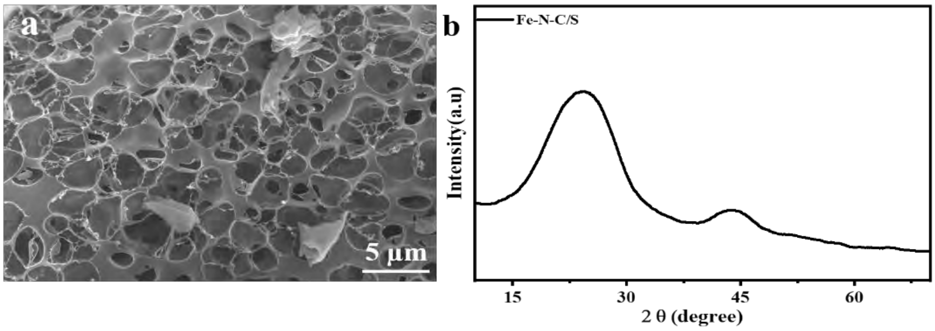

Figure 1. (a) SEM images and (b) xrd pattern for Fe-N-C/S

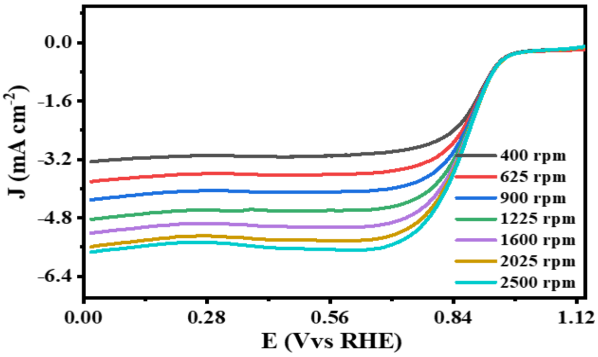

Figure 2. LSV at different rpm for Fe-N-C/S

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Highly dispersed PtZn intermetallic for efficient oxygen reduction catalysts

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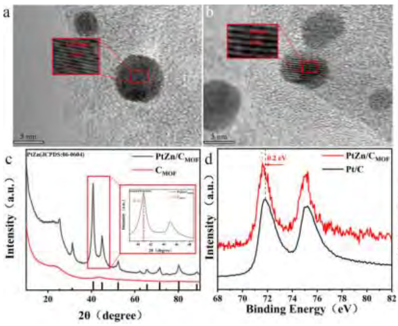
Abstract：This work develops a Zn-based MOF as catalyst support and provides a facile strategy to prepare atomically dispersed intermetallic alloys with highly activity and durability.



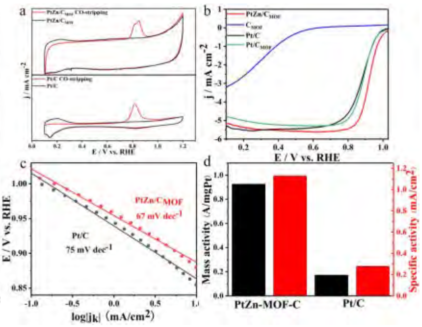


Figure 1. structure and composition of PtZn/C$_{MOF}$. **Figure2.** electrochemical performance of PtZn/C$_{MOF}$ and Pt/C.

Figure 1:

(a,b): lattice fringes of 0.221nm and 0.345nm are smaller than those(0.226nm, 0.351nm) of PtZn (111) and (220) facet, indicating the presence of lattice compression.

(c): XRD pattern of PtZn/C$_{MOF}$ agrees well with the intermetallic L1_0-PtZn PDF card(PDF#06-0604) without any impurity peak, indicating that the ordered L1_0-PtZn intermetallic alloy has been successfully formed. Slight peak position shifts to positive angle compared with standard pattern further demonstrate that the existence of compression strain makes lattice spacings smaller.

(d): Pt core levels(71.7eV of Pt4f) shows a 0.2eV negative shift to lower binding energies compared with Pt/C(71.9eV of Pt 4f).

Figure 2:

(a):The ECSA values for PtZn/C$_{MOF}$ and Pt/C are 81.9 and 60.1 m^2/g$_{Pt}$ respectively, demonstrating the higher ECSA and more active ORR potency for PtZn/C$_{MOF}$.

(b): The half wave potential E½ of PtZn/C$_{MOF}$(0.922V) is 42mV higher than commercial Pt/C(0.880V) observed from the linear sweep voltammetry (LSV) in a O_2-saturated 0.1 M $HClO_4$ solution.

Commented [1]: ？？？

(c): Tafel plot of PtZn/C$_{MOF}$(67mV/dec) derived from LSV exhibits smaller slope than Pt/C(75mV/dec), manifesting the enhanced kinetics for ORR.

(d): PtZn/C$_{MOF}$ delivers higher mass(0.926A/mg$_{Pt}$) and specific activities(1.13mA/cm^2) of Pt at 0.9 V versus RHE, which are respectively 5.4 and 4.0 times higher than those(0.172 A/mg$_{Pt}$ and 0.28 mA/cm^2) of the Pt/C reference.

Conclusion：

we adopt a facile one-step heat-treatment approach to obtain a series of highly dispersed PtZn intermetallic ORR catalysts based on a porous Zn-rich MOF. Small PtZn particles (mean size:3.95nm) enable large electrochemically active surface area(81.9 m^2/g$_{Pt}$) and high atomic utilization. The ligand effects and compressive strain optimize the Pt electron structure and binding strength between Pt and oxygen intermediates. These advantages result in better ORR performance (0.926 A/mg$_{Pt}$ of mass activity and 1.13mA/cm^2 of specific activity), which are respectively 5.4 and 4.0 times higher than those of commercial Pt/C(0.172 A/mg$_{Pt}$ and 0.28 mA/cm^2).

Electronic conductivity modification of $Na_3V_2(PO_4)_3$ cathode material using graphitic carbon shell for enhanced electrochemical performance

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NASICON structured sodium vanadium phosphate Na3V2(PO4)3 is a promising cathode material for rechargeable sodium ion batteries. The high specific capacity ~176.44mAhg-1 [1] and structural stability of Na3V2(PO4)3 are important characteristics for its application in sodium ionbatteries. We optimized nanostructured Na3V2(PO4)3 synthesis process and pristine and carbon coated Na3V2(PO4)3 material are prepared. Carbon coated Na3V2(PO4)3 was synthesized by varying carbon source molar fraction during sol-gel synthesis process. The refinement of X-ray diffraction measurements suggests the rhombohedral NASICON structure with R-3c space group. The measured lattice parameters are in agreement with the reported values [2]. The carbon presence has been confirmed using Fourier Transform Infrared (FTIR), Raman spectroscopic and thermogravimetric analysis (TGA) measurements. We will discuss the impact of electronic conductivity as a function of carbon fraction and its graphitic content in shell geometries with Na3V2(PO4)3 core, as explained in Fig. 1, on charge/discharge characteristics in hybrid coin cell structures, where lithium 'Li' metal has been used as anode material..

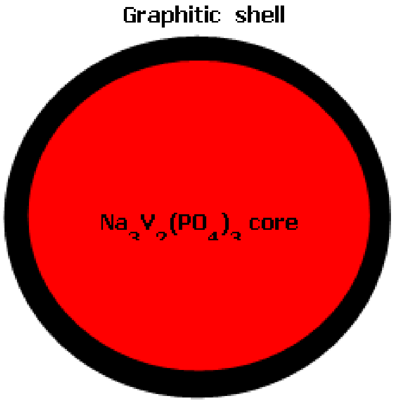

Figure 1. Schematic representation of graphitic carbon shell with $Na_3V_2(PO_4)_3$ core structure.

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Synchrotron X-Ray Analysis of Surface Modifications on *β*-Gallium Oxide to Control the Surface Conductivity and Chemical Reactivity

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Monoclinic beta-phase gallium oxide (*β*-Ga_2O_3) is a wide bandgap semiconductor (4.5-4.8 eV)[1] that possess the unusual combination of high visible transparency and high mobility *n*-type conduction, a class of materials called transparent conducting oxides (TCOs). There is considerable interest in this material for deep-UV sensing, high-frequency power electronics, and transparent sensor devices. *β*-Ga_2O_3 is also interesting from a fundamental perspective as its surfaces are different from those of other *n*-type TCOs such as ZnO, SnO_2, In_2O_3, and CdO.[2] The surfaces of the latter exhibit downward band bending and electron accumulation due to the presence of donor-like surface states, while *β*-Ga_2O_3 surfaces are characterized by upward band bending and electron depletion.[2]

Using electrochemical cyclic voltammetric and spontaneous methods, aryldiazonium ion, iodonium ion and phosphonic acid-derived organic films were successfully formed on the (-201) and (010) surfaces of *β*-Ga_2O_3. 2-4 nm multilayers of nitrophenyl (NP), methylphenyl (MP), and phenyl-based films were deposited using aryldiazonium salt and iodonium salt electrochemistry[3,4] whereas, monolayer octadecylphosphonic acid (ODPA) films were spontaneously formed by submerging the substrate in solution.[5]

Synchrotron X-ray photoelectron spectroscopy showed that all aryl modifications increased the upwards band bending by 0.5 eV at the Ga_2O_3 surfaces. Reduction of the nitro functionality was also induced by the synchrotron irradiation to form AP-like moieties and these layers further increased the upwards band bending by a further 0.1 eV. This corresponds to even more electron depletion at the surface which is highly unexpected. ODPA modification resulted in a decrease of the upwards band bending by 0.2 eV.

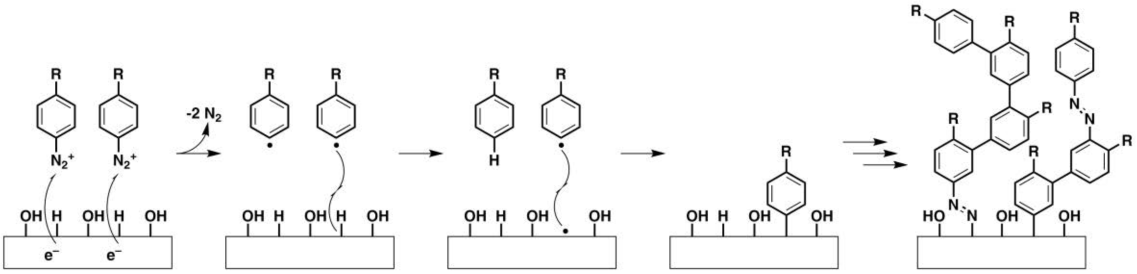

Figure: Electrochemical formation of aryl multilayers on *β*-Ga_2O_3 surfaces

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Electrochemically Assisted Polyamide Deposition at Three Phase Junction

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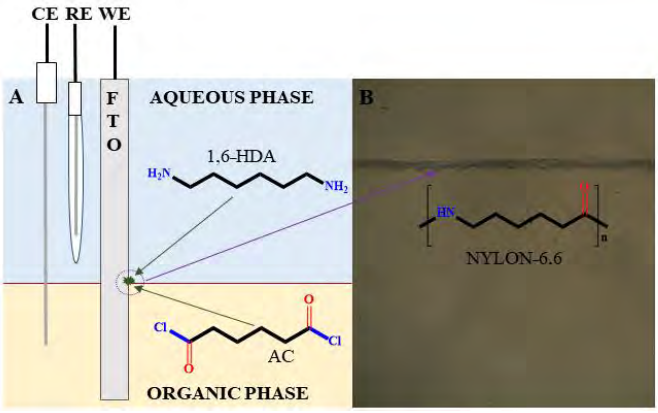
A three phase junction[1] formed between solid electrode placed between solutions of the organic phase and the aqueous phase is employed for localized and electrochemically assisted nylon–6,6 deposition. The fluorine doped tin oxide (FTO) conductive support (serving as the working electrode – WE) is immersed into the cell filled with two immiscible liquids. The aqueous phase (being on the top) contains 1,6–hexamethylenediamine (1,6–HDA) whereas the organic phase (being on the bottom) is a solution of adipoyl chloride (AC) dissolved in a 1,2–dichloroethane. The interfacial polycondensation reaction between these two reagents occurs spontaneously at the liquid–liquid interface at elevated pH and is inhibited when diamine is fully protonated.[2] This means that the local pH change can be used to control interfacial polycondensation reaction.

In this respect we have designed the electrochemical set–up shown in scheme 1A. Electrochemical processing is optimized together with a number of experimental conditions. The pH of the aqueous phase was adjusted in the range from 3.0 to 8.5 by the addition of 0.1M HNO_3 to a solution of 50 mM 1,6–HDA. Next we have studied the effect of the applied cathodic potential. Local pH increase was controlled by electrochemically formed OH^- ions at the WE surface only on the water side of the liquid–liquid interface. At pH > pK_a the diamine species deprotonates and are available to react with adipoyl chloride species from the organic phase. This reaction occurs only at the three phase junction and gives a polyamide strap formed at the WE in the very localized position (scheme 1B). We found that its dimensionality can be controlled by the experimental time, applied potential and pH of aqueous phase.[3]



Scheme 1. (A) A schematic representation of the electrochemical set–up used to decorate three phase junction system. (B) The optical microscope image of nylon–6,6 strap formed at the FTO electrode.

The control experiment was carried out in the same phase arrangement without the use of electrochemistry. The reaction of polyamide deposition does not occur spontaneously, no formation of nylon strap was observed even for elongated experimental times. An analysis of the obtained nylon–6,6 strap as further performed using IR spectroscopy, atomic force microscopy and scanning electron microscopy. This protocol will be extended to a number of polyamide based materials that can be applied in corrosion studies, sensing and smart materials development.

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A New Approach to Electrochemical Impedance Spectroscopy Fitting for Organic Semiconductors

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More and more, electrochemistry is becoming an everyman's tool. Researchers working in a variety of fields, such as biology, synthetic chemistry, or physics are starting to appreciate the relative low cost and versatility of electrochemical methods. With this emerging mass appeal, the amount of mistakes made in data collection and analysis is also increasing. In electrochemical impedance spectroscopy (EIS), where data analysis is especially complex, this can lead to significant misinterpretation of the results. After all, the knowledge required to design a representative equivalent circuit, comprising all the relevant components but avoiding misleading additions, is complex and can be a challenge even for experienced researchers. In addition, equivalent circuits only have limited flexibility and can struggle to represent less ideal electrochemical systems accurately.

We are developing a physics based EIS model for the analysis of organic semiconductor materials using COMSOL Multiphysics® software [1]. The design of the model will be guided by experimental results obtained for N,N′-di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB) and will endeavour to better understand the energy levels in organic semiconductor materials. While the scope of this model is relatively narrow, we believe that the general approach can be readily expanded and contribute to a better understanding of the physical properties in a range of organic semiconductors.

The poster will present some of our initial work and contrast results obtained using the physics based EIS analysis approach with standard equivalent circuit models in terms of ease of use, accuracy and computing time. The advantages and disadvantages of the two model systems will be discussed.

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Polymediators and Polyelectrolytes in Organic Electrosynthesis

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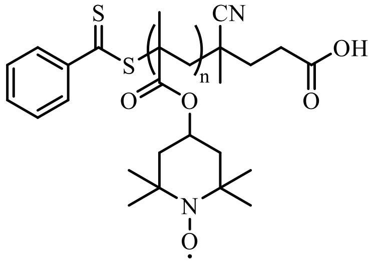
Although organic electrosynthesis is generally considered to be a green method, the necessity for excess amounts of supporting electrolyte constitutes a severe drawback. Furthermore, the employment of redox mediators results in an additional separation problem.[1] In this context, we have developed a polymer-based approach which allows for simultaneous separation and recycling of mediator and supporting electrolyte in a single step (see Figure, right) using membrane filtration. For this purpose, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and tetraalkylammonium groups were attached to a polymethacrylate backbone, resulting in well-soluble and task specific homopolymers **1** and **2** (see Figure, left).[2][3] Reversible redox behaviour was observed for the polymediator using cyclic voltammetry. The successful conversion of several test substrate using catalytic amounts of **1** demonstrated that such polymers can be applied for oxidation of alcohols under mild conditions. Furthermore, recyclability was demonstrated in preparative-scale electrolysis.[2]



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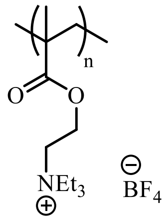

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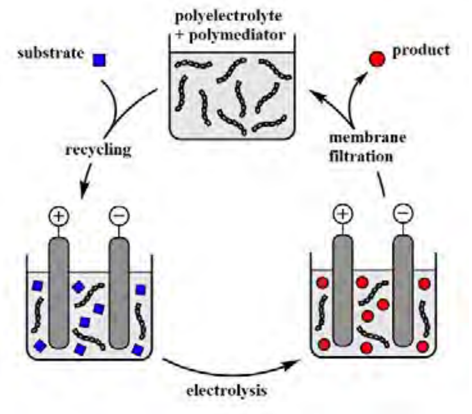

Since the electrolysis current is usually limited by diffusion of the redox-active species to the electrode, we are currently studying the influence of the molecular weight on current density for type **1** polymers. Our efforts are focused on finding a useful operating range in which an efficient membrane process, high current densities and optimum ionic conductivity can be achieved. RAFT polymerization allowed for the synthesis of polymers with well-defined molecular weight distribution between 3 and 100 kDa. We found that the redox-activity was increased with decreasing molecular weight, whereas the retention in the membrane filtration follows the opposite trend. Similarly, it is important to study the relationship between the ionic conductivity and molecular weight for type 2 polymers. A close investigation on polyelectrolytes' performance demonstrated that ionic conductivity is independent from the chain length.

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The Electrochemical Newman-Kwart Rearrangement under Microflow Conditions

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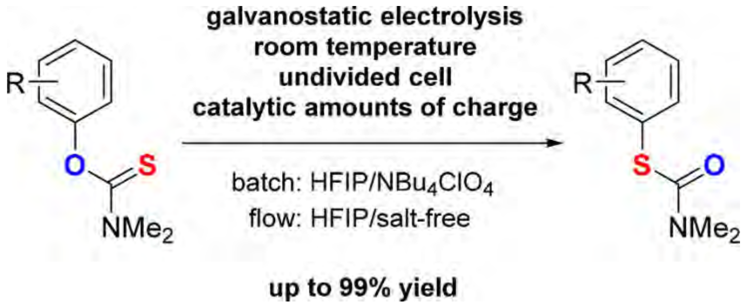
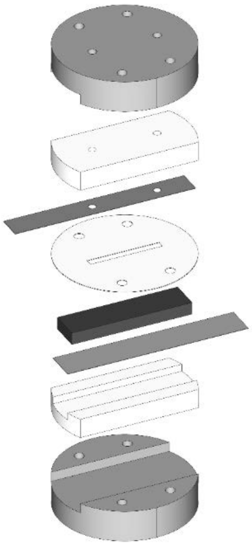


A common pathway for the synthesis of thiophenols is the three-step transformation of phenols via the Newman-Kwart rearrangement (NKR) of an *O*-aryl thiocarbamate to the corresponding *S*-aryl compound as a key step.[1,2] This rearrangement is thermally induced at temperatures up to 300°C. Via an electrochemical pathway we achieved this rearrangement at room temperature.[3] A mechanistic study revealed an electrochemically catalyzed pathway, in which anodic oxidation leads to a cation radical rearrangement,[4] thereby triggering a chain process in solution.[3] Furthermore, we investigated the effects of different substituents on the yield and side-reactions and identified the factors that govern the reactivity of specific substrates.[5]

In addition, we developed a procedure for an undivided microflow-reactor (see Figure, right), which allows for electrolysis without added supporting electrolyte. Since full conversion with quantitative selectivity is achieved, only a separation between the product and the solvent is needed. In the present contribution, the most important aspects of the electrochemical NKR under microflow conditions will be discussed.



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Determination of the pK_a of neutral molecular compounds in imidazolium-based ionic liquids

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Room temperature ionic liquids (RTIL) are one of the main alternatives to molecular solvents conventionally used for electrochemical applications such as electrosynthesis, energy conversion and storage devices, or electroanalysis [1]. In any of these applications, chemistry in solution in RTILs requires specific knowledge of the equilibrium processes because they partially define the success or failure of a given reaction. For this reason, it is imperative to know and control chemical parameters under imposed chemical equilibrium conditions, such as acidity levels via the pH parameter.

In this work, a study is presented to explain the acid - base phenomenon that occurs in certain RTILs in terms of the Brönsted - Lowry theory. With the information obtained, the changes in reactivity observed in some test compounds such as pyridine (Pyr) and N, N-dimethylethylamine (DEMEA) are explained.

A series of spectrophotometric and electrochemical assays were performed by potentiometry, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) at four different imidazolium RTILs: $[C_2mim][NTf_2]$, $[C_3mim][NTf_2]$, $[C_2mmim][NTf_2]$ and $[C_2Him][NTf_2]$; where C_2mm = 1-ethyl-3-methylimidazolium, C_3mm = 1-propyl-3-methylimidazolium, C_2mmim = 1-ethyl-2,3-dimethylimidazolium, C_2Him = 1-ethylimidazolium and NTf_2 = bis(trifluoromethanesulfonyl)imide. These RTILs were dried for 24 hours at 90 °C before use. Spectrophotometric assays were used to evaluate the effect of triflic acid (HOTf) on the protonation of a neutral molecular indicator (In) in solution in the RTILs [2,3]. For the electrochemical potentiometric assays, the open circuit potential (OCP) was determined, during a series of acid-base titrations, using as working electrode (WE) a modified interface $W^0|WO_{3(s)}$; Pt^0 was used as auxiliary electrode (AE) and several interfaces of the type $Ag^0|AgCl_{(s)}$, constructed and characterized previously by our research group [4], were used as reference electrodes (RE). Electrochemical assays by CV were used for dynamic determination of the pK_a for the conjugate acid-base pair (HA^+/A) of the test compounds [5,6]. For determination, a cell was used in a three-electrode configuration, using a modified Pt^0-Pt^0 interface as WE. All measurements were made under an inert and dry N_2 atmosphere and EIS was used to determine and compensate for the ohmic drop.

The spectrophotometric assays were used to determine the Hammett acidity parameter (H_0^0) and the pK_a value for the conjugate acid-base pair (HIn^+/In). On the other hand, the pK_a for the conjugate acid-base pairs of the test compounds (HA^+/A) was determinate by potentiometric titrations, using the OCP data obtained from the tungsten sensor, by fitting them to a family of Gunnar Grand functions and a complete titration function without segmentation. These values were also confirmed by CV. Finally, data were corroborated by the correlation of acidity scales with parameter H_0^0, showing differences of less than 2%.

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Activity and Stability Study of Iron Porphyrin Covalently Bound on the Surface for Oxygen Reduction Reaction Catalysis

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The oxygen reduction reaction (ORR) is a crucial part for fuel cell function to produce electricity on-demand. So as to improve the fuel cell efficiency, the slow kinetics of ORR on carbon electrode requires a catalyst. Non-precious metal catalysts (NPMCs) have gained increasing attention as a cheap alternative material to Pt. Among various NPMCs materials, molecular metal complex catalysts are attractive as they can be immobilized on an electrode surface. They can act as a model of pyrolysed NPMC materials, giving well-defined active sites and insights into the ORR catalytic mechanism. They also allow the possibility of structure control to achieve a leap in electrocatalyst efficiency and stability.

The stability of molecular metal complex catalysts, especially iron tetraphenylporphyrin (FeTPP), is an issue for catalyzing ORR in acid solution. Although a few studies have been done to investigate the degradation mechanism of pyrolysed NPMC materials,[1, 2] it is still not well-understood. Studying the composition change of the immobilized FeTPP film under ORR conditions can potentially lead to understanding of the degradation mechanism. Therefore, in this project, FeTPP molecule was immobilized on carbon surface via an axial ligand and also directly to the porphyrin ligand by electrografting from aryldiazonium salts. Electrochemistry, atomic force microscopy and X-ray photoelectron spectroscopy were used to investigate and compare the film structure change before and after ORR in acid aqueous solution. The potential degradation mechanism for FeTPP under ORR conditions will be proposed.

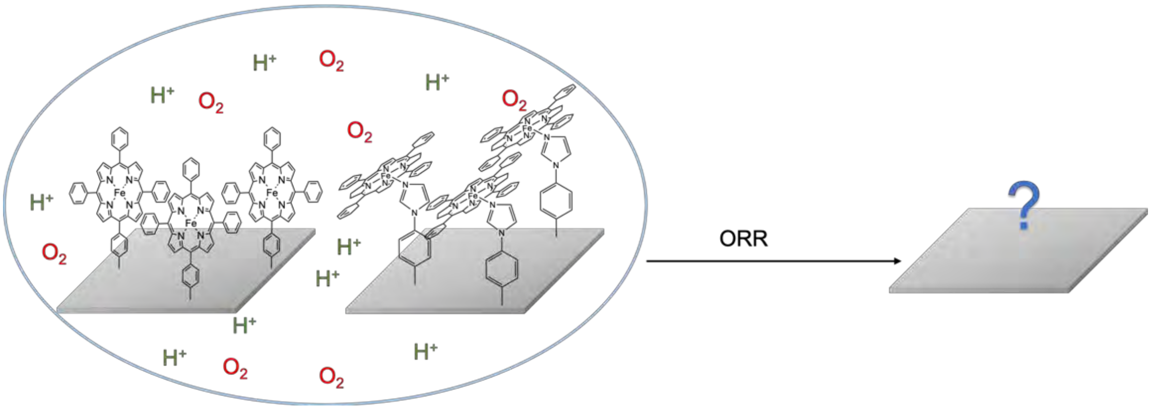

Figure 1. FeTPP film structure study as prepared and after ORR catalysis.

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Enhancement of electrochemical redox reaction by transition metal oxalates for high-performance lithium-sulfur battery

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As the growth of global EVs market and continuous advances of IT devices' functionality, higher capacity and cycle stability of secondary batteries are being demanded. Lithium-sulfur(Li-S) battery is one of the promising next-generation batteries due to high theoretical capacity(1,672 mAh/g), natural abundance, and environmental nontoxic compare to conventional active materials of lithium-ion batteries. However, lithium polysulfide(PS) dissolution issue which causes capacity fade inevitably must be overcome for commercialization.

In this study, we introduced metal oxalates synthesized with the first transition metal series as cathode additives. They have a high polar surface area which is able to enlarge the electrocatalytic interfacial boundary enabling LiPS redox reactions to occur. Furthermore, physicochemical interactions between LiPS and metal oxalates were verified by UV-vis, X-ray Photoelectron Spectroscopy, and Electrochemical Analysis(Cyclic Voltammetry, Galvanostatic Intermittent Titration Technique, Electrochemical Impedance Spectroscopy). As a result, the modified cathode by the best candidate effectively decreased cell overpotential and improved the cycle stability by maximized electrochemical sulfur utilization.

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Amorphous Ni-Mn_3O_4 electrodeposited on activated carbon for capacitive deionization

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With the population increasing, the available water resource in the world is diminishing. It has been predicted that by the year 2025, 60% of the world's population will face troubles accessing fresh water. This will affect not only the domestic sector but also the industrial and agricultural sector. The water that we use mostly come from fresh water resource, which is 2.5% of the total water on Earth. The other 97.5% is from saline water. As a solution for water scarcity, many countries like Saudi Arabia or the United Arab Emirates, use desalinated water as an alternative. Capacitive deionization (CDI) is an emerging desalination technology, which extracts the salt from water through electrostatic adsorption with an applied potential. CDI has numerous advantages. Its operation does not require high energy input since desalination can occur at low applied potentials. Moreover, it also does not require any additional chemical during the desalination process, which would lower down its cost compared to other desalination technologies. Even with its promising capabilities, CDI still has challenges in fabricating an electrode material that would have excellent performance and stability. Pseudocapacitive materials, primarily metal oxides, are potential CDI electrodes due to their excellent capacity and cyclability. In this study, different metal ratios of Ni-Mn_3O_4 was coated on activated carbon through anodic electrodeposition at constant current. The electrode surface was characterized using FESEM, XRD, BET and contact angle measurements. Its electrochemical performance was determined through CV and EIS analysis. The results from these measurements was used to pick the optimized Ni-Mn_3O_4. The chemical nature of the optimized deposit was analyzed through XPS and Raman spectroscopy. Using the fabricated electrode, it was paired with pristine AC to form an asymmetric CDI cell. At 1.2 V, it showed an excellent salt adsorption capacity of 8.54 mg g^{-1}, which is 2.5 times higher than a symmetric cell with AC. Moreover, it was able to retain 87% of its capacity after 50 adsorption-desorption cycles. Therefore, coating AC with Ni-Mn_3O_4 has successfully improved the CDI performance of pristine AC. The low cost of the metal precursors used for the electrodeposition will make it a potential material for large scale or commercial use.

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Reinforcing the durability of PtCo catalyst by including dissolved Co^{2+} capturing layer in PEMFC cathode

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Fuel cell is the energy system that converts chemical energy to electric energy, using hydrogen and oxygen. Among various type of fuel cells, proton exchange membrane fuel cell (PEMFC) operates in low temperature and its electronic density is high, thus it is known as one of the promising environmentally friendly energy systems. Since oxygen reduction reaction (ORR) in PEMFC has higher overpotential due to sluggish reaction kinetics, Pt-based metal catalysts are usually used as ORR catalyst. To enhance both ORR activity and price competitiveness, 4d transition metals (e.g. Co, Ni, Fe) have been commonly utilized by alloying with Pt. However, these transition metals are not thermodynamically stable as metallic state in the PEMFC operating condition such as pH, which causes the dissolution of transition metal and deactivation of PEMFC performance during repeated operation.

In this study, we tried to strengthen durability of the PtCo/C catalyst in PEMFC cathode. During PEMFC operation, Co^{2+} ion is dissolved from PtCo/C. To capture these Co^{2+} ion, we added N-doped carbon layer, consisting of mainly pyridinic N. We observed oxidation peak in cyclic voltammetry to confirm whether Co^{2+} is captured. Then, ORR performance was compared according to the amount of N-doped carbon. Also, accelerated stress test (AST) was conducted to evaluate the durability of catalyst with N-doped carbon.

Asymmetrical Electrode System for Large-scale Reverse Electrodialysis

Ji-Hyung Han

RED is an energy conversion system that generates electric power from a salinity gradient over ion-exchange membranes (IEMs) and is essentially pollution-free. In a large-scale one, the cathode is highly vulnerable to significant inorganic scaling due to the high pH conditions during water reduction and crossover of multivalent ions in the natural feed solution. We surmised that asymmetrical electrode system, where the geometrical area of the cathode is smaller than that of the anode, is a reasonable route to addressing the fouling issues. Because the minimized contact area between the electrode solution and feed solution by reducing the geometrical area of the cathode can decrease the amount of crossover caused by the non-ideal permselectivity of the IEM, uphill transport, and leakage, thereby decreasing the rate of precipitate formation or organic fouling. The change in the maximum power with varying area of the cathode was measured in lab-scale (100 cell pairs) and large-scale (1,000 cell pairs) RED systems to determine the minimum geometrical area of the cathode without significant power loss. It was confirmed that even though the area of the cathode corresponds to 60% of the area of an individual IEM, we can obtain the maximum power with only 3% of power loss in the large-scale RED stack. In addition, the asymmetrical electrode can be applied to a bipolar membrane (BPM)-RED system reported in our previous work. The high current density achieved by reducing the size of the cathode can induce vigorous water splitting in the BPM, which leads to more effective blocking crossover of the multivalent and hydroxide ions.

Nanostructured Cellulose Modified via Sulfonic Acid Crosslinking as a New Material for Proton Exchange Membrane

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Nanostructured cellulose (nanocellulose) is an attractive material platform for proton exchange membrane, however its application for this purpose is not widely explored. The use of nanocellulose membranes in PEMFCs was pioneered by our group and previous works have demonstrated that both cellulose nanofiber (CNF) and cellulose nanocrystals (CNC) membranes can be used as PEM in hydrogen fuel cells (FC). However, membranes made of pristine nanocellulose have quite low proton conductivity and lack the stability at high temperature and humidity. The proton conductivity of unmodified CNF membrane was ~0.05 mS/cm and ~4 mS/cm for unmodified CNC membrane [Bayer, T. et al., Chem. Mater. 2016, 28, 4805–4814] and therefore requires significant improvement to be considered for FC application.

Conventional approaches for cellulosic materials modification (e.g. backbone sulfonation) can achieve better proton conductivity, but with worsening of mechanical properties, aqueous, and chemical stability. In contrast, crosslinking of nanocellulose was shown to provide improved mechanical properties and reduced swelling in water [Quellmalz et al. ACS Biomater. Sci. Eng. 2015, 1, 271−276], as well as better proton conductivity when an appropriate crosslinking agent is used (i.e. strong acid) [Seo J. A. et al. Ionics 2009 15, 555–560].

In this work we use chemical crosslinking of different forms of nanocellulose with sulfosuccinic acid (SSA) in order to improve properties needed for PEM applications. Crosslinking of cellulose nanofibers (CNF) and cellulose nanocrystals (CNC) membranes was performed in a hot-press, to form SSA-x-CNF and SSA-x-CNC membranes. Initial tests demonstrated that membranes with 10-30 μm thickness can be conveniently produced. Crosslinked membranes showed significantly decreased swelling in water, stability in boiling water, and increased through-plane proton conductivity.

Our research findings confirm the hypothesis that a properly selected crosslinking molecule can turn nanocellulose into an effective proton conductor. Mechanical properties, aqueous and chemical stability can be improved simultaneously. Investigation into the effect of crosslinking on mechanical strength, chemical stability, proton conductivity and fuel cell performance are still underway and will be reported.

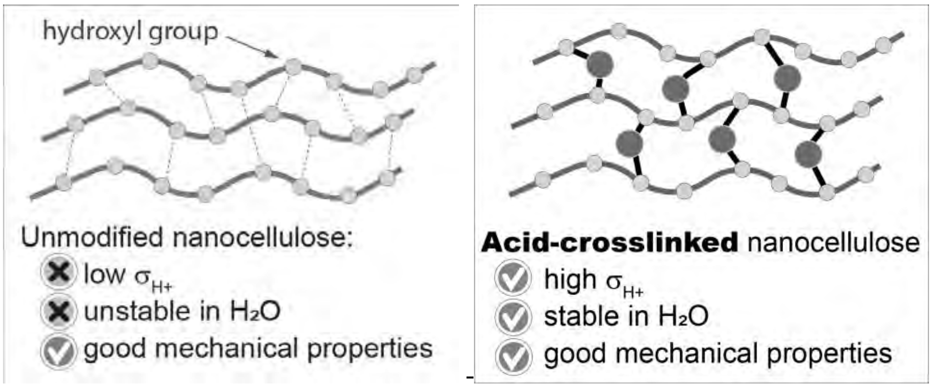

Figure 1. Schematic representation of the crosslinked cellulose material able to deliver useful properties for the PEM applications.

A membraneless and separatorless multiphase flow battery

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Storage of excess power generated via renewable sources, such as with wind turbines and solar plants, can help enable increased penetration of renewable sources into the electrical grid. Many flow battery (FB) chemistries have been investigated, and among them the zinc-bromine flow battery (ZBFB) is currently commercially deployed. The ZBFB exhibits favourable characteristics such as high open circuit voltage (OCV) of ~1.84 V, abundant and cheap reagents with bromine ~\$5/KWh and zinc ~\$2/KWh, and no requirements for precious metal catalysts. As the ZBFB operates in a closed loop form, the capacity of energy delivered during discharge is determined by the amount of electrodeposited zinc during charge. Traditionally, a membrane or separator divides an anode and cathode compartment, and the anolyte and catholyte flows. However, membraneless and separatorless cells offer simplified single flow operation and reduced cell cost. Several strategies for membraneless and separatorless cells have been investigated, namely laminar flow separations, utilization of immiscible electrolytes, use of complexing agents, and metal-based electrolytes.

Bromine complexing agents (BCA), such as quaternary ammonium bromide (QBr) salts, are example of electrolyte additives that sequester the bromine to form a separate dense polybromide phase[1], thereby enabling membraneless operation. After complexation, the concentration of active bromine in the aqueous phase is reduced by as much as two orders of magnitude. Since the sequestered bromine is phase-restricted, its diffusion towards the zinc electrode, which is the primary mechanism of self-discharge and of zinc corrosion, is significantly decreased. Such QBr are recognized also as controlling the zinc dendrite formation and growth at the zinc electrode[2]. Yet the addition of BCA comes at a cost, primarily blocking of surface reaction sites[3] and lowering the OCV[4].

We here report on a membraneless and separatorless ZBFB, which relies on a single, multiphase flow between the anode and cathode. The flow is an emulsion, consisting of a continuous, bromine-poor aqueous phase and dispersed particles of bromine-rich organic phase. We characterize the cell performance experimentally, including polarization curves, plating efficiency, and round trip energy efficiency. We elucidate key mechanisms behind the enhanced performance of this battery, demonstrating that increasing organic phase fraction allows for enhanced current capability.

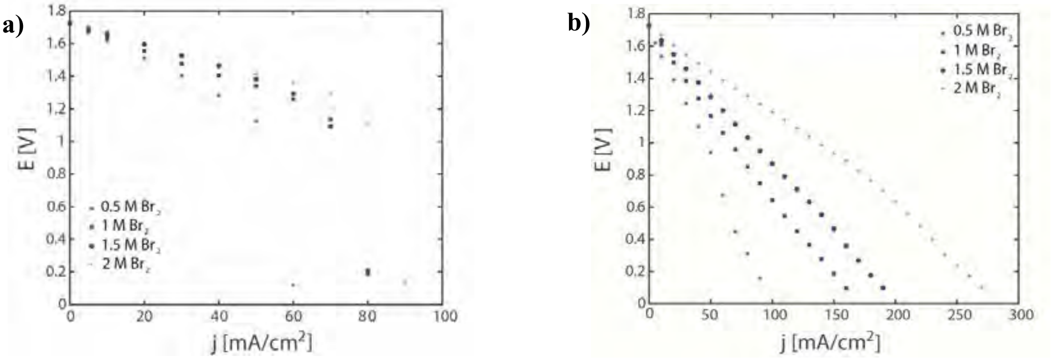

Figure 1. At varied SOC **a)** limiting current without BCA and **b)** limiting current with BCA.

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Photocurrent measurement from the controlled monolayer deposition of photosynthetic reaction center proteins on a gold surface

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The photosynthetic reaction centre (RC) from *Rhodobacter sphaeroides* has been extensively studied for use in biohybrid solar cells. Much of the previous work has focussed on improvements of photocurrent generation, with currents reaching up to several uA. The basis behind these improvements was loading the electrode surface with many copies of the protein resulting in multilayers. The primary disadvantage with this approach is the random orientation of proteins, with some supposedly oriented properly. Rather than use this existing approach, we used RCs with Cys for covalent attachment to a gold electrode and for proper orientation. Areas of bare electrode surface and RCs bound non-specifically (i.e. not bound via the Cys) were competitively displaced by an insulating, non-redox layer of mercaptohexanol (MCH). We were able to determine through adsorption isotherm measurement that a single monolayer of RCs was produced, with the surface not covered by RCs passivated with an MCH blocking layer. The adsorbed monolayer of RCs was imaged using atomic force microscopy to detail the distribution of RCs on the gold surface for surfaces prepared with different RC deposition concentrations. Photocurrents were measured for all RC modified surfaces using a LED modulation method which enabled measurement of photocurrent in the presence of large faradaic currents at a variety of applied potentials.[1] The photocurrents generated from a monolayer composed of RCs and MCH resulted in much larger currents than without an MCH blocking layer. The rate of electron transfer generated via photoexcitation was measured with applied overpotential and a reorganization energy was determined. Our approach is different from established methods, in that instead of loading the electrode surface with multilayers, we built a single monolayer. Preparing a well-defined single monolayer is a superior approach for fundamental studies compared to maximising protein loading on the surface for consistent photocurrent generation.

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A Desloratadine Voltammetric Sensor Based on Carboxymethyl-Botryosphaeran Stabilized MWCNTs Aqueous Dispersion

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Desloratadine (DESL) is a third-generation selective antihistaminic drug that functions as a H1-antagonist of histamine on cell receptor sites and is used to treat allergic symptoms without causing sedation. Severe side effects reported reinforce the need of simple, low cost, and precise methods for the determination of this drug. Voltammetric methods meet these requirements with multi-walled carbon nanotubes (MWCNTs) extensively being used to modify electrodes since, as a nanostructured material, present electrocatalytic features due to their high surface area and electron mobility [1]. The procedure of preparing and using MWCNTs as an electrode modifier is based upon their suspension/dispersion in a specific solvent before drop casting onto the electrode surface. Recently, polysaccharides were discovered that increase the water dispersive capability of carbon nanostructures [2]. In this sense, the polysaccharide carboxymethyl-botryosphaeran (CMB) was used to improve the dispersion of multi-walled carbon nanotubes (MWCNTs) in water, and this feature was applied in the modification of a glassy carbon electrode (GCE) to obtain a sensitive voltammetric sensor for the determination of DESL. CMB was obtained by the carboxymethylation of botryosphaeran, an exopolysaccharide produced by the fungus *Botryosphaeria rhodina* MAMB-05 [3]. The voltammetric measurements were performed in a three electrodes-arrangement electrochemical cell and a PGSTAT 101 potentiostat/galvanostat supported by NOVA 2.1.4 software. The supporting electrolyte of voltammetric measurements was a 0.10 mol L^{-1} KH_2PO_4 solution with the pH adjusted to 8.0 with 2.0 mol L^{-1} NaOH. The 1 mg mL^{-1} dispersion of MWCNTs in water was obtained in the presence of 1 mg mL^{-1} of CMB. An aliquot of 20 μL of this dispersion was dropped-cast into a polished-surface of a GCE and dried at room temperature. The morphology and spectroscopic behavior of the sensor were evaluated. SEM images of the unmodified and modified GCE indicated that CMB wrapped the MWCNTs allowing it to disperse into water due to the amphiphilic properties of the derivatized polysaccharide. The dispersion led to the formation of a homogeneous film on the GCE surface. The electroactive area of the modified sensor increased 53% compared to the unmodified GCE. Electrochemical impedance experiments showed that the addition of MWCNTs to GCE caused a drastic decrease (97%) in the charge transfer resistance, and after the incorporation of CMB, this resistance increased 28%. Initial exploratory studies revealed that DESL does not present an electrochemical response on the unmodified GCE in a potential scan from 0 to +1.4 V using cyclic voltammetry, but on the modified sensor, an irreversible anodic peak was observed at 1.15 V. The sensor preparation was uniform and the relative standard deviation of the DESL peak current obtained using three different modified electrodes was 1.12%. The oxidation of DESL was pH-dependent and the mechanism involves one proton and one electron. Linear sweep voltammetry was employed for the construction of the analytical curve. Different scan rates were tested, and statistically confident results were achieved using 25 mV s^{-1}. In this condition, the modified sensor presented a sensitivity of 1.018 μA L μmol^{-1} in the linear working range of 1.99–32.9 μmol L^{-1}, with a detection limit of 0.88 μmol L^{-1} of DESL. In addition, the sensor showed excellent repeatability with a relative standard deviation of only 1.02% over a sequence of 10 measurements. The selectivity was checked analyzing the influence of the presence of compounds present in the sample matrices in the current of DESL and no significant interference was observed at a ratio of 1:10 (DESL:interfering agent). The sensor was successfully applied in the analysis of pharmaceutical preparations containing DESL (tablets and oral solutions), with equivalent results compared to a validated spectrophotometric method at the 95% confidence level. The sensor was also employed in the analysis of a spiked sample in rat serum with recovery percentages ranging from 100 to 105%. The results confirmed that the MWCNTs and CMB modified GCE used in conjunction with the linear sweep voltammetry technique presented satisfactory performance in the determination of DESL in pharmaceutical and biological samples.

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Energy Efficiency and Mechanisms of Hot Carrier Transfers in Plasmonic Photoelectrochemical Reactions of Small Organic Molecules on Silver Electrodes of Nanostructures

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The main problem in plasmon-mediated chemical reactions (PMCR) is how to promote the energy conversion efficiency of light energy to chemical energy. This low energy conversion efficiency is due to the ultrafast relaxation of surface plasmon resonance (SPR) and hot carriers generated from the SPR on metal nanostrucutes. In order to obtain the deep insight in the relationship of PMCR and SPR in metal surface of nanostructures, we investigate the chemical reaction processes of small organic molecules adsorbed silver electrodes. Here the laser is used to excite surface plasmon on silver nanoparticles modified silver electrodes. The small organic molecules are p-aminothiophenol (PATP) and 8-bromoadenine (8BrAd). The first molecule can be related to the hot hole oxidation process while the second molecule does the hot electron induced C-Br bond cleavage on the silver electrodes of nanostructures. The electrochemical surface-enhanced Raman spectroscopy was used to record the evolution of surface species under laser irradiations.

Our experimental results provide a pathway to connect photonic absorption and photoelectrochemical kinetics on surface SPR hot spots, which confine incident far field light to nanoscale surfaces and generate high energetic electrons and holes. From the time-dependent SERS signals and absorption spectroscopy, we can estimate the apparent rate constants of chemical reactions, such as the transformations of PATP to p,p'-dimercaptoazobenzene (DMAB) and 8BrAd to adenine adsorbed on silver electrodes of nanostructures, which can exhibit the strongest surface Raman signals. By combining the experimental results and density functional theory calculations, we provided the reaction mechanisms that describe well the role of the hot carriers driven chemical reactions. Now we use the quantum yield to estimate the energy conversion efficiency of chemical reactions due to the photogeneration of hot carriers, which involved to the SPR effect. The energy efficiency is still low close to 1%, which can be modulated by excitation wavelengths and applied potentials.

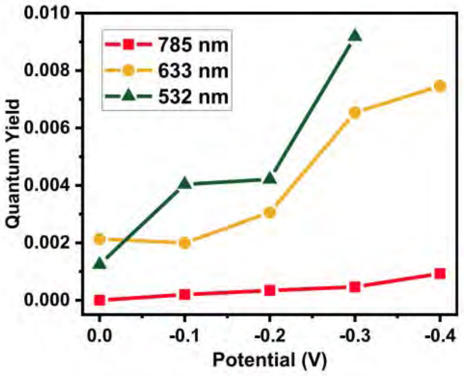

Figure 1. Quantum yield for energy conversion efficiency of PMCR in silver nanoparticles modified silver electrodes

Incorporating a Film of β-Glucan onto a Carbon Black Modified Electrode: A New Architecture for Sensing of Cyclobenzaprine

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The application of nanomaterials for the development of new electrochemical platforms has received a great deal of attention due to the capacity of improvements in the signal/noise ratio, mass transport and catalytic behavior [1]. Carbon black (CB) is an example of a nanomaterial used to develop new electrochemical sensors. For improved adhesion, CB can be incorporated into a polysaccharide film, in this case, the β-glucan named botryosphaeran (BOT). Thus, the purpose of this work was to develop a novel architecture based upon a modified glassy carbon electrode (GCE) with CB onto a film of BOT (CB-BOT/GCE) for the voltammetric determination of cyclobenzaprine in pharmaceuticals, tap and lake water, and synthetic plasma. For modification of GCE, CB was first dispersed in dimethylformamide (2 mg mL^{-1}). After polishing the GCE surface, an aliquot of the CB dispersion was pipetted onto the surface of GCE concomitantly with a 3 µL solution of BOT (0.78 mg mL^{-1}) and allowed to dry for 3 h at room temperature. The modification of the GCE caused an increase in the electroactive area and electrochemical impedance spectroscopy showed an improvement of the electron transfer rate on the modified electrode surface compared to the unmodified GCE. The electrochemical behavior of cyclobenzaprine was investigated using cyclic voltammetry in a KCl solution resulting in an anodic peak at 0.97 V vs. (Ag/AgCl (3.0 mol L^{-1} KCl)). It was not possible to observe a reduction peak on the reverse scan, suggesting that cyclobenzaprine undergoes an irreversible reaction. The fabricated electrode showed a better analytical response, higher current magnitude, and lower oxidation potential for cyclobenzaprine, when compared to unmodified CGE or GCE modified only with CB or BOT. The concentration of CB in DMF was studied changing the amount of CB (1.0 – 3.0 mg mL^{-1}), with the highest current obtained using 3.0 mg mL^{-1}, but due a better repeatability of 2.0 mg mL^{-1} (relative standard deviation (RSD) = 1,64%), this concentration was chosen for subsequent analysis. NaCl solution (0.1 mol L^{-1}) was chosen as the supporting electrolyte for the determination of cyclobenzaprine. The voltammetric peak current obtained for 50 µmol L^{-1} cyclobenzaprine was observed over the scan rate range of 5 – 250 mV s^{-1}. The anodic peak current varied linearly with the scan rate, suggesting that the cyclobenzaprine redox process on the surface of CB-BOT/GCE was adsorption-controlled. The number of electrons (*n*) transferred in the oxidation of cyclobenzaprine on CB-BOT/GCE was estimated from the equation $E_p – E_{p/2} = 47.7$ mV/α*n*. The E_p and $E_{p/2}$ values were respectively, 0.98 and 0.91 V, where *n* in the oxidation of cyclobenzaprine was estimated to be 1. Following the optimization of the parameters of the square-wave voltammetry (SWV) and differential pulse voltammetry, the analytical curves were built using both techniques, due to better linear adjustment, higher sensitivity, and lower limit of detection (LOD), SWV technique was chosen for the determination of cyclobenzaprine. The anodic peak currents for cyclobenzaprine increased linearly with the concentration in the range of 2.0 to 20.6 µmol L^{-1}, following the regression equation $I/\mu A = -1.55 + 8.05 \times 10^5$ [cyclobenzaprine/mol L^{-1}] ($R^2 = 0.998$), with a LOD of 0.028 µmol L^{-1}. Lastly, the modified electrode was successfully applied for the determination of cyclobenzaprine in real samples of pharmaceutical products, whose results were statistically similar to those obtained using a volumetric method at a confidence level of 95%. The cyclobenzaprine concentration was also determined in tap and lake water, and in synthetic plasma with an average recovery of 98.2%. The results confirmed that the CB-BOT/GCE used in conjunction with the SWV technique presented a satisfactory performance in the determination of cyclobenzaprine in pharmaceutical, water, and biological samples.

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Electrochemical study on the endogenous redox rhythm in cyanobacterium *Synechococcus elongatus* PCC7942

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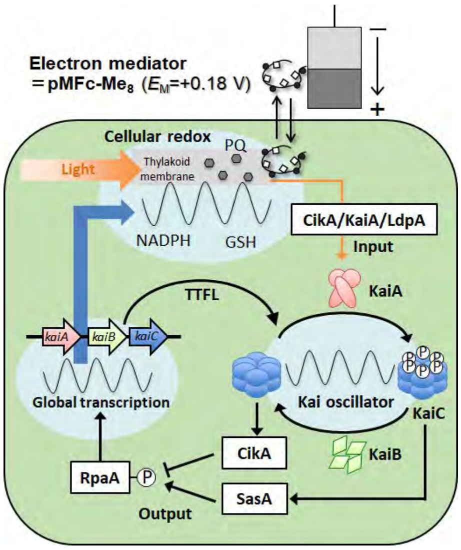
In photosynthetic organisms, intracellular redox changes depending on the environment, which leads various acclimation processes in a cell. Thus, real time monitoring of intracellular redox of photosynthetic organisms is important for understanding their physiology. We have developed an electrochemical system which enable real time monitoring of intracellular redox by using a membrane permeable electron mediator: pMFc-Me_8 (Fig. 1). This method has applied to various organisms including photosynthetic microbes [1-3]. pMFc-Me_8 is comprised of 2-methacryloyloxyethyl phosphorylcholine (MPC) unit and ferrocene unit. MPC-based polymers are known to exhibit high cytocompatibility due to their protein adsorption resistance, which allows long time scale measurement of intracellular redox. Importantly, redox potential of the ferrocene unit (the mid-point potential (E_M): +0.18V vs. SHE) is adjusted to the level to that of plastoquinone (E_M: +0.1V), which enables us to monitor the redox change of photosynthetic electron transport chain *in vivo*.

In this study, we adapted this method for studying circadian clock, which is one of the photo-acclimation functions equipped in cyanobacterium *Synechococcus elongatus* PCC7942 (*S. elongatus*). The medium containing pMFc-Me_8 and *S. elongatus* cells was injected into an electrochemical cell with indium-tin-oxide (ITO) working electrode and Ag/AgCl reference electrode. The electrochemical assay revealed that intracellular redox of *S. elongatus* cell exhibited circadian rhythms under constant light conditions. When the transcription and translation of *kaiABC*, which are the essential clock genes [4], is defunctionalized, the redox rhythm disappeared. This fact indicated that the transcription and translation controlled by the KaiABC oscillator generates a circadian redox rhythm. It is noteworthy that the amplitude of the redox rhythm at a constant light condition was large enough to affect the KaiABC oscillator [5]. Based on this finding, the intracellular redox state in *S. elongatus* is supposed to actively controlled to change in a 24-h cycle under constant light conditions by the circadian clock system.



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Modeling of Multi-Ion Transport in Shock Electrodialysis

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Shock electrodialysis (SED) is a new water treatment method invented and developed by the Bazant lab. SED applies an over-limiting electric current through a membrane-sandwiched, slightly charged microporous material, which will induce a deionization shock and split the crossing stream into a fresh and a brine stream at the outlet. The process is continuous, and its energy requirement diminishes significantly for dilute feed solution. Desalination by SED was demonstrated early on, but it was only recently that we discovered the ability to continuously and selectively remove certain ions (mostly multivalent) from water, which indicate that SED has the potential to effectively remove trace toxic metal ions (mostly multivalent) from drinking water and industrious water at a very low cost, compared with other traditional water treatment methods which lack selectivity.

However, the selective ion removal by SED has not been well understood yet. Experimental data indicated that in most cases SED prefers to remove multivalent ions, but a counter example is the selective removal of K^+ from seawater. Moreover, the total desalination and ion removal selectivity can be dependent on various variables, such as current, feed component, surface chemistry, and geometry. Therefore, we want to develop models to help understand the multi-ion transport in SED. Though there have been simple models to roughly predict desalination of binary electrolyte system, it's the first time that multi-ion transport in SED has been modeled. In this work we have developed two models for multi-ion transport in SED: a traditional macroscopic model which solve for homogenized quantities in porous media, and a depth-averaged microscopic model for 3D planer channel. The latter one is able to include the pore-scale profiles, which may differ for different ions and lead to selective ion removal. We will use the two models to test various conditions, and evaluate the SED performance in terms of total desalination and ion removal selectivity. We will compare the results with our experiments and learn the mechanisms of selective ion removal, and then use the model to explain the experimental data and help optimize the experiments.

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Effect of secondary solution concentration on lithium electrodialysis using lithium ion electrolyte $Li_{0.29}La_{0.57}TiO_3$

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The demand for lithium resources is rapidly increasing with the production of lithium-ion batteries. Today's lithium is produced from brine or ore [1]. The issues of the former are long process time and large environmental burdens. The latter issue is the high cost for high purification [2]. To establish a better lithium recovery method, we have investigated lithium recovery by electrodialysis using lithium ion conductive solid electrolyte $Li_{0.29}La_{0.57}TiO_3$ (LLTO). The electrochemical impedance of electrodialysis is affected by the concentration of cations in solution. When this recovery is performed in a batch system, the lithium ion concentration of the solution changes as the recovery of lithium proceeds. Therefore, it is important to elucidate the influence of the lithium ion concentration in the solution on the electrochemical impedance. In this study, we investigate the effect of lithium ion concentration in the secondary solution on lithium recovery rate by electrodialysis using LLTO.

An anode (primary side) and a cathode (secondary side) electrodes were prepared on the surface of LLTO using a platinum paste. Reference electrodes was prepared on both surfaces of the LLTO at positions apart from the anode and cathode. A DC voltage of 2.0 V was applied between the anode and cathode. Electrochemical impedances were measured by the 3-terminal method using the reference electrodes and 2-terminal method. The primary side solution was a 1.0 M aqueous lithium hydroxide solution. The secondary side solution was pure water or an aqueous lithium hydroxide solution having a concentration of 10^{-3}-1.0 M. The amount of transferred lithium was estimated by Faraday's law using the current value.

As shown in Figure 1, the migration rate of lithium depended on the concentration of lithium ions in the secondary solution and reached a maximum at 10^{-2} M. The cause of this dependence was clarified by the AC impedance method.

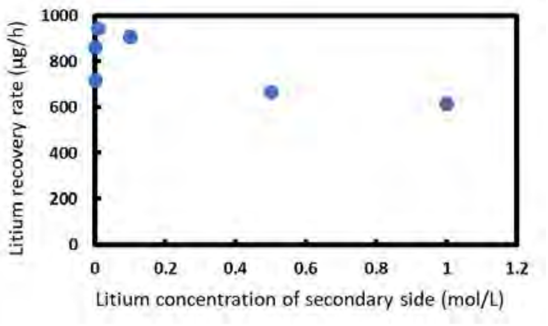

Figure 1 Lithium recovery rate at different lithium concentration in electrodialysis secondary solutions.

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Comparison of kinetics and degradation mechanism of two isomers by electrochemistry

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Dimethylphenols (DMPs) are one of the main organic compounds in the environment and annually are discharged 730,000 tons in the water environment, which are threating water quality. DMPs have six isomers, among which 2,4-Dimethylphenol (2,4-DMP) is listed as a priority by the US Environmental Protection Agency due to its high toxicity and 2,6-Dimethylphenol (2,6-DMP) also has long-term adverse effects on the aquatic environment. In this study, the differences in current density and hydroxyl radical utilization between the two isomers were compared. Besides, the intermediate products and degradation paths of two isomers were analyzed and discussed by in-situ FT-IR spectroscopy. The purpose of this study was to compare the electrolysis information of 2,4-DMP and 2,6-DMP in various aspects and revealed the influence of the position of the methyl on the benzene ring on the electrolysis conditions. It will provide a theoretical basis on the isomers pollutants of electrolytic in the future.

Fig. 1a showed that at the current density of 4.5mA cm^{-1}, the (kinetic constants) K of 2,4-DMP was 0.0049 min^{-1} and that of 2,6-DMP was 0.0166 min^{-1}, indicating that the degradation rate of 2,6-DMP was quicker than that of 2,4-DMP. Fig. 1b showed that the intensity of 2,4-DMP was higher than that of 2,6-DMP by electron spin technique (ESR) spectrometry, indicating that fewer hydroxyl groups were used in the electrochemical reaction of 2,4-DMP and the degradation rate was lower at the same current density. As shown in Fig.2, the main intermediate products of 2,4-DMP and 2,6-DMP pollutants were different. The main macromolecular intermediates of 2,4-DMP were 2-Methoxy-4-methylphenol (ethers) and a few of ketone, alcohols, carboxylic acids, while those of 2,6-DMP include 2,6-Dimethylbenzoquinone (quinones) and 5-Hexen-2-One (ketone) mainly and few of carboxylic acids. The open-loop voltage were both at 1.4V. As a result, the position of the group on the benzene ring of pollutants had significant influence on electrochemical information.

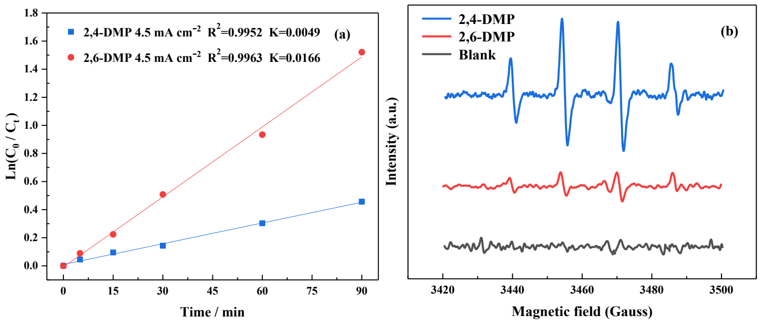

Fig. 1. Influence of pollutant structure on current density: (a) kinetic analysis, (b) •OH radicals utilization. (Ti/PbO_2 electrode, pH =5.8, Na_2SO_4 =0.1 mol L^{-1}; initial DMPs concentration =100 mg L^{-1}).

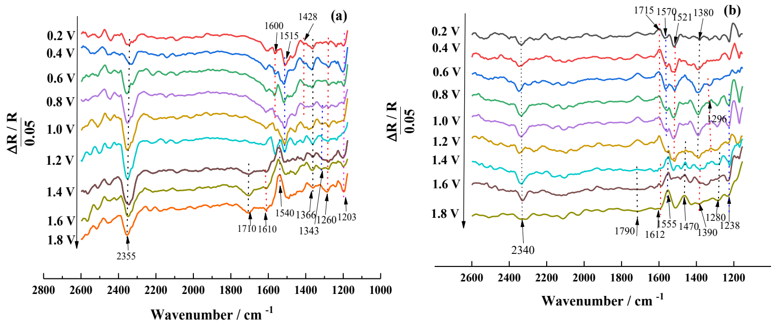

Fig.2. FTIR spectra collected for Ti/PbO_2 electrode, and the sample potential was stepped from 0.2V to 1.8V:(a) 2,4-DMP pollutant;(b) 2,6-DMP pollutant (Na_2SO_4=0.1mol L^{-1}; DMPs concentration=100 mg L^{-1}; pH =5.8;50 interferograms, p-polarised light, reference potential 0 V) .

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Conductivity change due to crack generation in zirconium oxide film

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We are studying covering the surface of the structural material of the divertor for thermonuclear fusion reactor in contact with the liquid metal with the corrosion resistant film. Here, the corrosion resistant film is a film that has compatibility with liquid metals and excellent high heat load resistance performance. In the case of the surface of the structural material facing the plasma is made of metal zirconium, if the zirconium surface is oxidized to be a corrosion-resistant film, it can have not only excellent compatibility and high heat load resistance performance, but also hydrogen-permeation prevention property. Furthermore, because zirconium oxide containing lattice defects at oxygen sites has oxygen ion conductivity, it is theoretically possible of in-situ diagnose of changes in the microstructure of the film due to changes in the conductivity characteristics measured by the AC impedance method. In this study, we measure the AC impedances of a dense oxide film prepared by the self-oxidation method in water vapor and an oxide film that has cracked by rapid thermal cycling (100 °C/h). Comparing with microstructure change observed by scanning electron microscope, we try to clarify the possibility of in-situ diagnosis by microstructure change by conductivity measurement *via* the AC impedance method.

Figure 1 shows cross-sectional SEM images of the zirconium oxide film (a: as prepared by the self-oxidation method, b: after rapid thermal cycle treatment). The zirconium oxide film prepared by the self-oxidation method was dense. By the rapid thermal cycle treatment, cracks with a width of about 1 μm and many small cracks were generated in the film parallel to the interface between the film and the Zr plate. Figure 2 shows Nyquist plots of the electrical conductivity measurement results in thickness direction of each film. After the crack was generated, the conductivity could be measured by AC impedance method, but the resistance increased 2.5 to 3.0 times of the dense film.

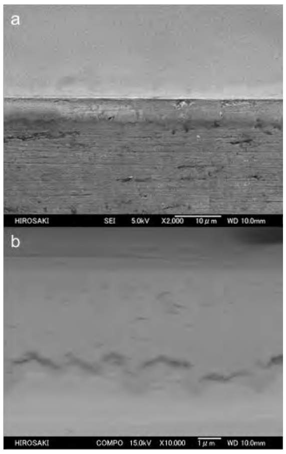

Figure 1. Cross-sectional SEM image of oxide film formed on Zr plate surface. a: as prepared film, b: after rapid thermal

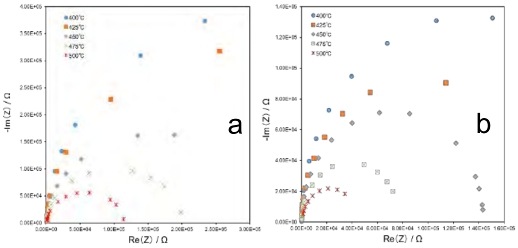

Figure 2. Electrical conductivity of oxide film by AC impedance method (Nyquist plots). a: Dense film after film formation, b: Crack-introduced film by rapid thermal cycle treatment.

Spectroelectrochemical Study of Phenol Oxidation on Platinum Electrode

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Electrochemical oxidation is an effective way for the wastewater treatment due to its advantages of non-selectivity, highly controllability. Electrochemical in situ spectroscopy (FTIR), a real-time method, has been gradually used to study the mechanism of electrochemical oxidation/reduction in a molecular level. In this work, mechanism of phenol electro-oxidation was studied by cyclic voltammetry and in-situ FTIR on platinum electrode.

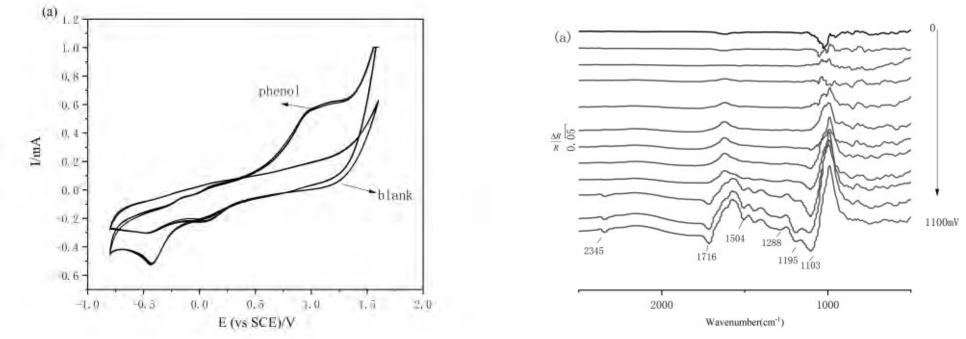

Fig. 1 Cyclic voltammetry (a) and in situ FTIR spectra (b) of phenol on Pt electrode surface

During the anode potential scanning, the oxidation of phenol appeared at 900 mV in contrast with the blank, showing that Pt electrode exhibited a high electrochemical activity for the oxidation of phenol. The bands appearing on the calculated spectrum was studied with variation of potentials (from 0 to 1.1V). The phenol degradation process was investigated and proved by several positive bands. Negative-going band appeared starting from potential 0.9 V, the intensity of which reached the most at 1.1 V. Negative-going band at 1103 cm^{-1} is assigned to the group of alcohol. Bands at 1288 cm^{-1}, 1716 cm^{-1} and 1504 cm^{-1} belong to the group of acid and carboxylate. Ketone and CO_2 were observed at 1195 cm^{-1} and 2345 cm^{-1}, respectively. Meanwhile, the result of GC-MS is consistent with the assignment of byproducts produced in FTIR experiment. All the results indicated that phenol can be thoroughly oxidized on Pt and the deduced mechanism is credible.

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Additives for Low Temperature Performance of Na_2SO_4-Polyacrylamide Electrolytes

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Aqueous-based polymer electrolytes are key enablers for solid-state electrical double layer capacitors (EDLCs) that are inherently safe with thin and flexible form factors. Polymer electrolytes comprised of Na_2SO_4-polyacrylamide (PAM) were developed with high ionic conductivity, good chemical stability, and wide voltage window at ambient conditions. However, its ionic conductivity and ability to form EDLC were severely degraded below 0 ˚C due to the formation of crystal hydrates below the freezing point.

In this study, dimethyl sulfoxide (DMSO) was investigated as an additive, leveraging its deep eutectic properties with water, to improve the low temperature performance of Na_2SO_4-PAM. Various amount of DMSO was added into Na_2SO_4-PAM and its effects on the material and electrochemical properties under ambient and sub-zero temperature were assessed. Raman microscopy revealed electrolyte films with homogenous and chemically compatible mixture. The electrochemical performance of Na_2SO_4-PAM at ambient temperature was minimally affected by DMSO. Meanwhile, the addition of DMSO enhanced the ionic conductivity Na_2SO_4-PAM below 0 ˚C (Fig. 1a) and allowed its enabled cells with activated carbon electrodes to maintain near-rectangular CV profile at -10 ˚C (Fig. 1b). Thus far, DMSO has been demonstrated as a good additive to widen the operating temperature range of Na_2SO_4-PAM.

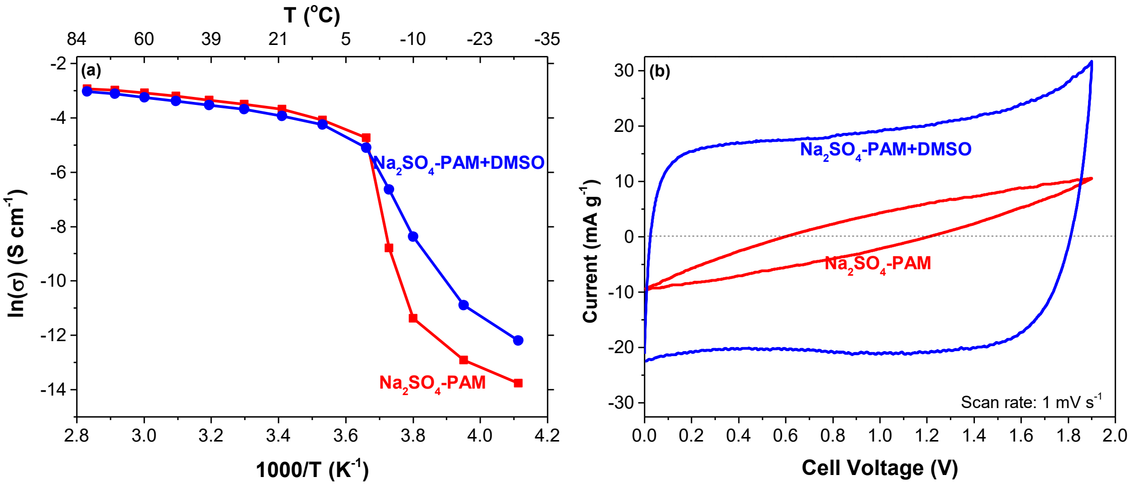

Figure 1: Comparison in performance of Na_2SO_4-PAM+DMSO vs Na_2SO_4-PAM on their (a) ionic conductivities (Arrhenius plot) and (b) CV of activated carbon devices (-10 °C, 1 mV s^{-1})

Electrochemical Properties of CVD Graphene on Copper Substrate

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Highly Oriented Pyrolytic Graphite (HOPG) as also real graphene sheets have surfaces with heterogeneous electrochemical properties according to the structure of sites: basal, edge, defect in the basal site etc. Each type of sites has own electrochemical activity with different Butler-Volmer terms and cyclic voltammetric profiles of a given redox pair [1]. However, there are also other important electrochemical processes as the evolution of hydrogen and electrodeposition on the graphene surface. Growth of graphene using the CVD method (so-called CVD graphene) on mono- and polycrystalline copper surfaces give the possibility to obtain large-area graphene coatings [2]. The μ-Raman Spectroscopy (μ-RS) is very sensitive on the properties of graphene layers and this method enables the possibility to characterise the following main properties of CVD graphene: (i) number of layers of graphene coating; (ii) type and density of defects, (iii) deformation/stresses in graphene coating and (iv) doping charge. Simultaneously, this method permits the determination of some deposition products as tin and tin-zinc alloys as also their changes during formation processes. The relatively large areas of sample can be analysed on the base of a set of spectra from the small areas (about 1 μm^2 in used experimental conditions). This allows the formulation of statistical description, and a graphical representation of the distribution of heterogeneity of graphene layers in micro-areas simultaneously with the description of deposition products. The surface topography and roughness of the substrates were examined using atomic force microscopy (AFM, tapping mode). The examinations of the electrodeposition processes were done using copper, tin and tin-zinc alloys on the copper substrate covered by CVD graphene. The processes of the electrodeposition of Cu, Sn and Sn-Zn layers as also hydrogen evolution from citrate solutions on graphene/copper substrate were investigated and optimal parameters were determined. The obtained results indicate a strong influence of defects in CVD graphene materials (types, density), an important role of substrate preparation (topography, roughness, oxidation) and influence of electrodeposition conditions on the properties of the graphene layers. The damages of graphene coatings by the evolution of hydrogen were analysed by μ-Raman Spectroscopy and optical microscopy (Fig.1). The electrodeposition of tin on such damaged layers appears selective deposition of tin only on the not damaged graphene layer and lack of tin on the uncover copper surface (Fig. 2). The electrodeposition of tin-zinc alloys gives similar results. The results of E-pH diagrams calculations for Cu-H_2O, Cu-SO_4^{2-}-H_2O etc. in experimental conditions were presented and electrochemical processes on graphene/copper surfaces were conducted potentiostatically for chosen and different E-pH parameters where Cu, CuO, Cu_2O, Cu_2O-B_2O_3 (in borate buffer environment) were dominant compounds. The surfaces of samples after potentiostatic experiments were investigated by AFM, μ-RS and OM. The CVD graphene protects the copper surface against oxidation except some areas contain the defects in the graphene layer.

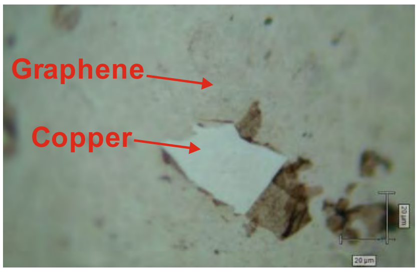

Fig. 1. The damaged layer of CVD graphene by the evolution of hydrogen

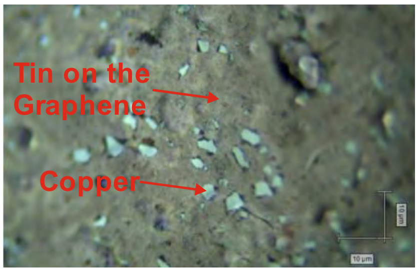

Fig. 2. The selective deposition of tin only on the not damaged graphene layer

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Synergistic Effect between Pt Active Sites and Readily Oxidized Secondary Metal in Partially Disordered Pt-M Electrocatalysts for Methanol and CO Oxidation

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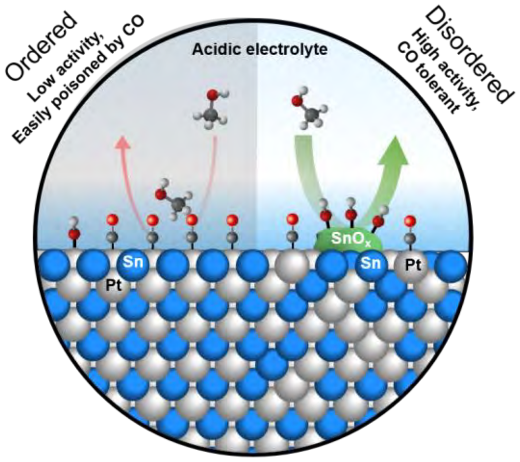

Synergistic effect between Pt or Pd active sites that adsorb CO and metal oxides of less noble metal that dissociate water to form OH_{ad} is commonly regarded as the reason bimetallic catalysts outperform pure-metal catalysts in processes that include CO oxidation.[1] It has been shown that alloy catalysts shorten the distance between sites for CO_{ad} and sites for OH_{ad} into sub-nano range and are effective in oxidizing CO at much lower overpotential than non-alloyed catalysts with similar compositions.[2] To answer whether the highest intimacy between atoms of Pt and secondary metal in the ordered configuration could further enhance the activity, we modify the degree of ordering of Pt_3Sn nanocubes while maintaining the exposed {100} facets to exclude the influence of exposing facets.[3] Strikingly, the 60% ordered Pt_3Sn nanocubes outperform the 95% ordered Pt_3Sn nanocubes for the methanol oxidation reaction by almost 5 times when considering the charge of the oxidation peak in the anodic direction of the cyclic voltammograms. The onset potentials of methanol oxidation and CO oxidation using the 60% ordered Pt_3Sn nanocubes is about 150 mV more negative than those using the 95% ordered Pt_3Sn nanocubes. Moreover, we demonstrate the outstanding tolerance to CO of less ordered Pt_3Sn nanocubes comparing to the 95% ordered Pt_3Sn nanocubes by saturating the electrolyte with CO during methanol oxidation. XANES spectra suggests that the d-band structures of the Pt in different degree of ordering are quite similar, whereas the XPS spectra reveal that the Sn at less ordered configuration are easier to be oxidized under the oxidative potential during methanol oxidation reaction, which provides more abundant OH_{ad} in the vicinity of Pt-CO that boosts CO oxidation. This model system shows that ordered alloys are not always more active than their disordered counterparts, and CO oxidation via the Tafel-Heyrovsky mechanism is more facile on the disordered phase of alloy catalysts.

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Synergistically Electronic and Structural Engineering of Electrocatalysts towards Advanced Electrochemical Water Splitting

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The increasing concerns on severe environmental issues and rapid fossil fuel depletion stimulate the intensive interests in renewable and sustainable energy sources. Hydrogen energy through electrochemical water splitting is considered as one of ideal options to feed energy demand without environmental concerns. The challenge for its commercialization is to minimize the electricity consumption and cost, which requires the efficient, low-cost and durable electrocatalysts for hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode.

The catalytic performance of electrocatalysts are closely related to the intrinsic activity and the number of the accessible catalytic sites in the electrocatalysts. This presentation will focus on the exploration of earth-abundant efficient HER and OER electrocatalysts with an emphasis on the performance boosting by the synergistic engineering of catalyst structures. Several reasonable strategies will be introduced for rationally engineering the morphological structure, electronic structure, and crystalline structure of electrocatalyst to augment the accessible catalytic sites and boost their intrinsic activity, leading to the significant performance enhancement of these low-cost materials for practical applications.[1-3] These results will open opportunities for the rational design and bottom-up synthesis of cost-effective and high-performance electrocatalysts for sustainable hydrogen production through electrochemical water splitting.

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Iron-Containing Porphyrins Self-Assembled on ZnO Nanoparticles as Electrocatalytic Materials for Oxygen Reduction

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Nonprecious metal electrocatalysts (NPMEs) have been recognized as highly promising oxygen electroreduction catalysts, but improving their activity and stability in acidic electrolyte remains critical. The use of porous materials with high specific surface area is one of the most direct and effective ways to increase their activity. Here, we integrated self-assembly technology induced by rotary evaporation with the hard-template method to synthesize Fe-N-codoped NPMEs with large specific surface areas and hierarchical pore structure. The presence of Fe^{3+} dramatically decreased the carbonization temperature of the precursors and the vaporization temperature of carbothermally reduced zinc, which is beneficial for both the in situ growth of micropores/mesopores within the carbon layers and the retention of more nitrogen-containing groups. Meanwhile, iron atoms present in the obtained Fe-N-C/ZnO electrocatalyst established FeNx ORR active sites. The obtained Fe-N-C/ZnO porous carbon material exhibited outstanding oxygen reduction reaction catalytic activity with $E_{1/2}$ of 0.78 V (vs. RHE), along with respectable electrochemical stability in a perchloric acid electrolyte (only a 7 mV negative shift after the durability test). Applied in fuel cells, the electrocatalyst loading was reduced to 2.0 mg/cm^2 because of increased mass transfer arising from the hierarchical porous structure and resulting in a power density of 700 mW/cm^2. The significantly improved activity and durability are contributed by the hierarchical porous structure and direct 4e$^-$ ORR mechanism of NPMEs.

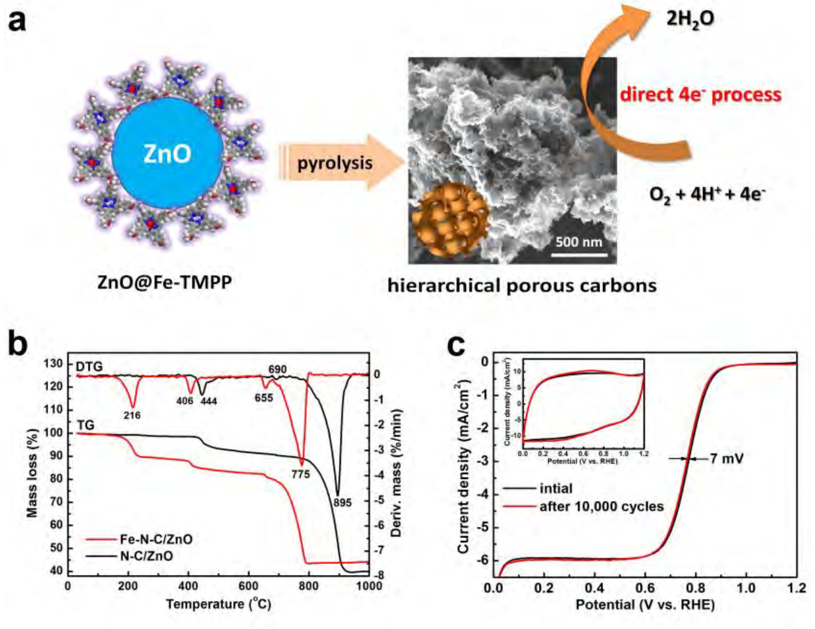

Figure 1 (a) Schematic synthetic process of porous carbon materials; (b) TG and DTG curves of precursors collected in N_2; (c) ORR polarization curves and CV curves (inset) measured before and after the durability test (0.6-1.0 V, 10,000 cycles).

A New Electrochemical Sensor Based on Oxidized Capsaicin/MWCNT/GCE for Xanthurenic Acid, Ascorbic Acid, Dopamine, Epinephrine and Uric Acid Quantification

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Chemically modified electrodes have been developed and present advantages, such as low price, portability and good analytical performance for the detection of target analytes [1]. In the present case, capsaicin (CAP) was used as a redox mediator and added to multi-walled carbon nanotubes (MWCNT) modified glassy carbon electrode (GCE). The CV profile for the oxidation of CAP is displayed in figure 1A, together with the possible oxidation mechanism (Fig. 1B). The presence of the redox system (IIa/IIc) is important for the redox catalysis, which can be understood through the formation of carbocation, which undergoes hydrolysis with the formation of quinones, responsible for the reversible system [1,2] (Fig. 1B). This modified platform was applied for the determination of xanthurenic acid (XA), ascorbic acid (AA), dopamine (DA), epinephrine (EP) and uric acid (UA), one at a time, using cyclic voltammetry (Fig. 1C) and chronoamperometry, in buffered aqueous solutions, pH 7.0. The diffusion coefficients (*D*) for XA was obtained as 5.67 x 10^{-5} cm^2 s^{-1}; for AA, 1.23 x 10^{-6} cm^2 s^{-1}; for DA, 6.97 x 10^{-4} cm^2 s^{-1}; for EP, 4.00 x 10^{-5} cm^2 s^{-1} and for uric acid, 3.0 x 10^{-5} cm^2 s^{-1}The obtained analytical curves for XA, AA, DA, EP and UA showed linear ranges, between 10–95, 5–75, 5-115, 50-1150 and 5–70 μmol L^{-1}, respectively. The detection limits were 8.76, 1.95, 1.80, 7.20 and 1.56 μmol L^{-1} for XA, AA, DA, EP and UA, respectively. The catalytic constants for the oxidation of XA, AA, DA, EP and UA on the modified electrode were 5.94 × 10^4, 1.45 × 10^4, 3.12 x 10^5, 2.41 x 10^4 and 2.10 × 10^3 L mol^{-1} s^{-1}, respectively. This oxidized capsaicin-based platform is reported for the first time and is able to detect the analytes at a micromolar level.

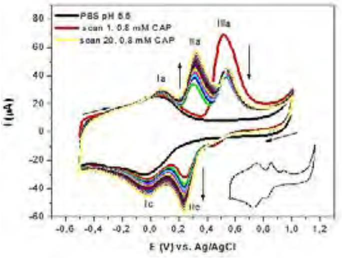

Fig.1 CV for capsaicin oxidation

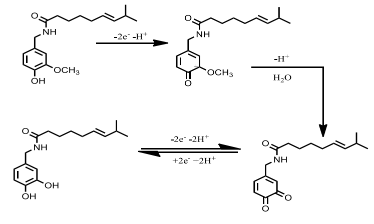

Fig.2 Mechanism for capsaicin oxidation

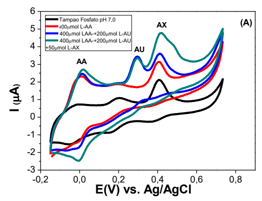

Fig.3 Electrocatalytic activity

for AA, AU and XA

Acknowledgements: To CNPq, CAPES/RENORBIO, FAPEAL, INCT-Bioanalítica.***e-mail of main author:** andresanjinho@hotmail.com **Ref.** [1] L.V. da Silva et al., Journal of Electroanalytical Chemistry 827 (2018) 230–252; [2] L.V. da Silva et al., Microchemical Journal 133 (2017) 460–467.

Full Cell Design Consideration for Uniform Lithium Distribution in Lithium Metal Rechargeable Battery

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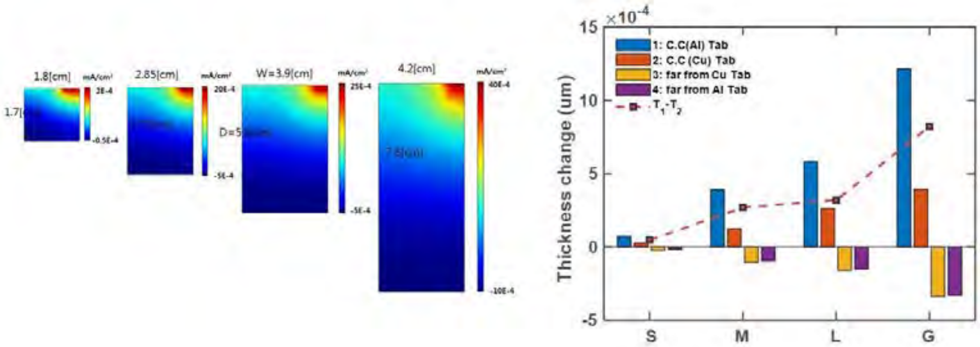
In a Li-metal rechargeable battery, it is critical to prevent the formation of dendritic or “dead” Li and stabilize the interface between the Li-metal and the electrolyte. Electrolyte composition, surface protective layer, and/or three-dimensional Li host structure are expected to play an important role for improving Li-metal anode performance. However, how to control the nonuniformity of current distribution and the corresponding spatial difference in Li volume change in a Li-metal anode can be another big issue once the Li-metal anode is operated under large areal cell format. Therefore, new strategies for uniform Li plating and stripping throughout the large Li-metal area are required in addition to the well-studied microscopic interfacial material designs for practical application of Li-metal rechargeable battery. This work exhibits relationship between Li uniformity and cell design factors in a large areal pouch cell format, and potentially promising strategy for improving the Li uniformity by changing cell component design, for example, current collector for Li-metal anode, which was simultaneously studied by mathematical modelling and experimental methods. These findings provide new perspectives for the design of large areal Li-metal rechargeable batteries needed for the practical application.



<Fig. 1. Mathematical modelling on Li-metal thickness change after 1 cycle in various cell size format>

Expansion of the potential region for the sustained discharge of non-aqueous Li-O_2 batteries by surface modifications of the positive electrode

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Non-aqueous Li-O_2 batteries are one of the next-generation batteries, which has a much higher theoretical energy density than the state-of-the-art Li-ion batteries. However, due to non-conductivity of Li_2O_2 formed on the cathode as the discharge product, the capacity is limited to be much smaller than the theoretical value. There are two different paths, surface and solution paths, for the Li_2O_2 formation, the latter of which is advantageous for the sustained discharge of Li-O_2 batteries.[1] It is now known that (1) positive electrode potential is a critical factor determining the reaction path, and (2) there is an optimal potential window where the solution path becomes dominant.[2] Considering the above facts, in this study, I aimed to expand the potential window for the sustained discharge by modifying the surface of the positive electrode.

Figs. 1(a) and (b) show discharge profiles at various potentials obtained for pristine carbon paper (p-CP) and surface-modified carbon paper (m-CP) positive electrode, respectively.[3] Surface modification of the CP was conducted by immersing p-CP in a hot acid (H_2SO_4:HNO_3 = 3:1) for 2 h. For the p-CP, the discharge capacity exceeded 100 mAh/g_{carbon} at 2.2 and 2.4 V, whereas it was less than 10 mAh/g_{carbon} at 1.8 and 2.0 V. This indicates that the discharge reaction occurred via surface and solution paths at lower and higher potentials, respectively. Almost no cathodic current was obtained at 2.6 V on the p-CP. On the contrary, for the m-CP, large discharge capacity in the range between 80 and 100 mAh/g_{carbon} was obtained at all potentials examined. It should be noted that a large discharge capacity was obtained even at 2.6 V (Fig. 1c). Thus, it was revealed that the potential window for the sustained discharge could be expanded by the surface modification of the CP.

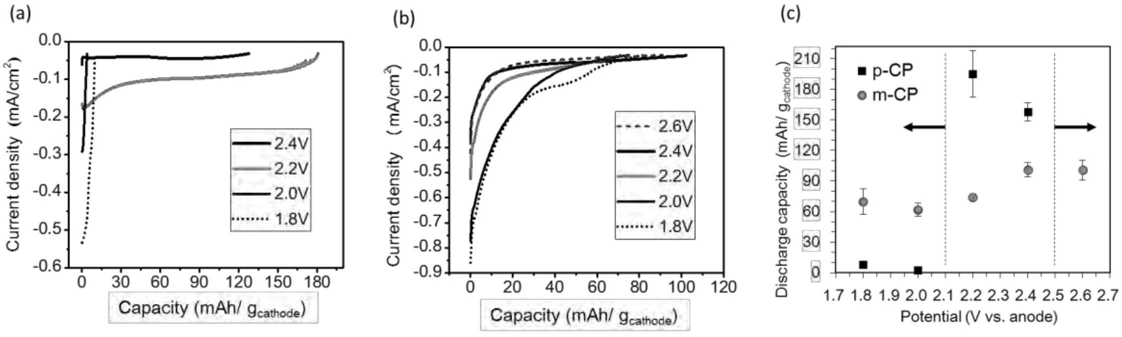

Figure. 1 Discharge profiles at various positive electrode potentials for (a) p-CP and (b) m-CP. (c) Discharge capacity vs. potential plots for p-CP and m-CP.

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Incorporation of FDU-12 mesoporous silica towards enhancement of carbon paste electroanalytical properties

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Mesoporous silica FDU-12 presents applications in several fields of science, including food and environmental analysis, pollutant adsorption, catalysis, drug delivery, enzymatic immobilization, nanoscience, biotechnology, and recently in the field of immunology with advances towards the research of vaccines and oral vaccines, but there are few reports about the use of this material on sensors development.(1,2) In this work, FDU-12 structures were synthesized in acidic medium using tetraethoxysilane (TEOS), Pluronic 127 (triblock polymer),1,3,5-trimethyl benzene as a porous expander, and KCl as a catalyst.(3) The materials were characterized using Thermogravimetry, SAXS, and Nitrogen Adsorption Isotherm. The specific area of two synthesized materials was evaluated using BET methods ($602m^2/g$ and $700m^2/g$) and these materials were used to prepare carbon paste modified electrodes (FDU-12/CPMEs). The experimental conditions to obtain a very reproducible carbon paste (graphite/oil ration; order of the reagent additions; homogenization method and presence of humidity) were primarily optimized for the construction of the modified electrodes, which contained 74.1% of graphite, 18% of nujol 7,9% of FDU-12 concerning the total paste content. The FDU-12/CPME behavior was evaluated using cyclic voltammetry with $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ as an electrochemical probe. The presence of the FDU-12 in the composition of the modified electrode improved the performance of the electrode: increase in the current peak levels, maintenance of the cathodic and anodic peak potentials until υ values as high as $1Vs^{-1}$ and a subtle shift on the oxidation peak potential to the less positive potential, Figure 1. The improved performance of the modified electrode resulted from the synergic effects between high surface area and good mesoporous structuration of the silica FDU-12.

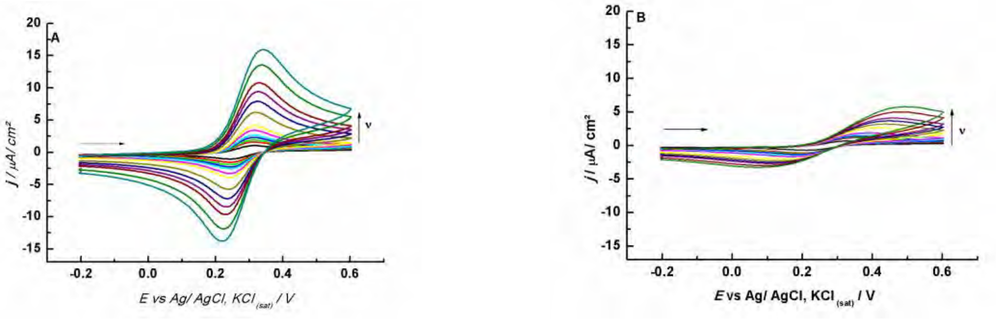

Figure 1. Cyclic voltammograms obtained with: **(A)** (FDU-12/CPME) and **(B)** CPE in 0.5mM of $[Fe(CN)_6]^{3-}$ plus 0.5mM $[Fe(CN)_6]^{4-}$ in 0.5M KCl, at υ from 10 to $1000mVs^{-1}$.

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Electrochemical synthesis, characterization, and antibacterial activity of copper based nanocomposite.

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Copper nanoparticles (CuNPs) are considered as potential antimicrobial agents due to their improved stability and safety, and longer active period than that of organic nanomaterials, with multi-targeted mechanism of action [1]. Nevertheless, metal NPs can suffer from agglomeration, reducing their antibacterial activity [2]. Cu incorporation in inorganic substrates such as metal oxides or montmorillonite (MMT) plays an important role due to the possibilities of creating an antibacterial nanomaterial with slow release of Cu species in order to obtain a prolonged antibacterial activity. Therefore, CuNPs were synthesized via a rapid electrochemical method using the inorganic micro-powders as carrier. Characterization studies on the nanocomposite were done by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The as-prepared Cu-based nanocomposites could be employed for inhibiting the growth of biofilms.

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Acknowledgements

Financial support is acknowledged from European Union's 2020 research and innovation program under the Marie Sklodowska-Curie Grant Agreement No. 813439.

On the investigation of the influence of surface crystallography and local packing density on the stability of thiolated DNA SAMs

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The stability of DNA self-assembled monolayer (SAMs) on gold electrode has drawn great attention in the biosensing field.[1,2] The performance and the lifespan or stability of the fabricated biosensor determine the reliability of the test results in early disease detection and point-of-care use.[3,4] The thermal stability of a mixed SAMs composed of a short alkythiol and alkythiol modified DNA prepared at OCP (open circuit potential) on a single crystal gold bead electrode were studied. These SAMs were carefully evaluated in buffer using in-situ fluorescence microscopy and electrochemical measurements. The single crystal bead electrode enabled study of a number of surface crystallographies in a self-consistent manner. For a selection of surface crystallographic regions, the stability and the functionability of the SAMs were studied after thermal treatment from 25 °C to 95 °C for 2 hours in buffer. The analysis showed that surfaces with hexagonal symmetry (111, 311, 211) were less stable than those with rectangular or square symmetry (110, 100, 210) which suggests that the characteristics of the surface should be carefully considered when using for sensor application. It was also observed that the packing density of the SAMs influences thermal stability since high DNA coverage slows the kinetics of thermal desorption which is beneficial for making more stable sensor. However it has been shown that low coverage DNA SAM has shown to be optimal for effective biosensing[5] and it seems to be challenging to make DNA SAMs with both low coverage and high thermal stability by using current SAM preparation protocols. In this study, we found that using potential assisted deposition can help to achieve DNA SAMs with both higher thermal stability than those made at OCP and with a good control of surface coverage. This study may help to explain the inconsistent results from the DNA SAMs during the experiments while the solution was heated[6] and provides valuable insights on improving the DNA biosensor preparation method in order to optimize the stability and the functionability at the same time.

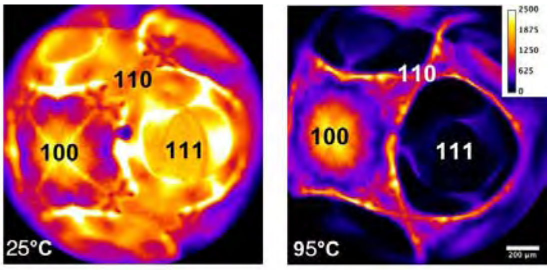

Figure 1: An example of the thermally induced changes in the fluorescence images of the single crystal gold bead electrode for a MCH/DNA SAM. The sample was prepared by 90 min in 1 mM MCH and 24 hrs in 1.0 µM DNA at 25 °C. The images were taken in buffer after the thermal treatment from 25 °C to 95 °C. The selection of crystallographic map is provided to guide interpretation of the images.

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Pb- and Bi-Modified Pt Electrodes toward Glycerol Electrooxidation in Alkaline Media. Activity, Selectivity, and the Importance of the Pt Atoms Arrangement

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The necessity for greener energy sources has been the major driving force in fuel research during the last decades, and it has driven the production of renewable fuels, such as biodiesel, from which glycerol is generated as a co-product. Glycerol is one of the several organic molecules which can be used in the cogeneration of electricity and platform chemicals in fuel cells, or in the simultaneous generation of hydrogen gas and chemicals in an electrolysis cell, a strategy called paired electrosynthesis (1). In this context, the main goal of our work is to develop Pt-based electrocatalysts for the electro-oxidation of glycerol (EOG) in alkaline media. In this work, we study the effects of the modification by Bi (2) and Pb (3) adatoms on both polycrystalline and single crystals of the main crystallographic orientations. In both cases, we found that adding the metal ions to the electrolyte resulted in the highest improvement of catalytic activity. The experiments with single crystals showed that the EOG activity on all facets was improved, with the (110) orientation showing the highest increase in current density (figure 1). *In situ* FTIR revealed that both adatoms block the adsorption of CO on Pt and suppresses the pathways in which C-C bonds are broken, seen in a reduction of the carbonate bands (2,3). Further investigation with online HPLC confirmed this observation, evidenced by the significant enhancement in the glycerate production (figure 2). We ascribed these results to a stabilization of several reaction intermediates through an interaction between its hydroxyl groups and the positively charged adatoms (4). We are currently studying the effect of other p-block adatoms to understand how each of them influence the electrode activity and the reaction selectivity.

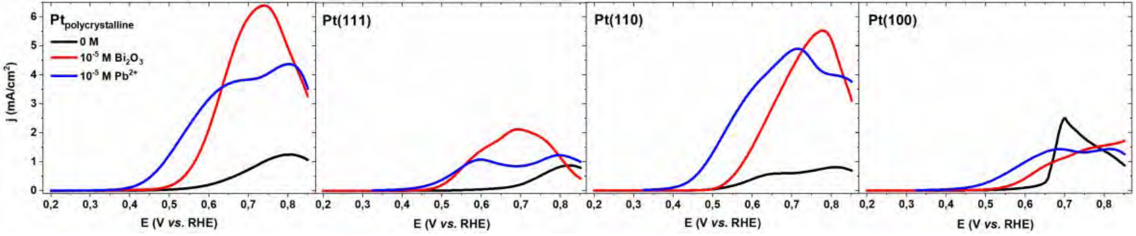

Figure 1: Effect of adding Bi (red) and Pb (blue) to the electrolyte during the EOG on Pt electrodes. Base electrolyte composition was 0.1 M NaOH + 0.1 M glycerol with addition of either 10^{-5} M Bi_2O_3 (red) or 10^{-5} M Pb^{2+} (blue). Scan rate was 10 mV/s. Adapted from (3).

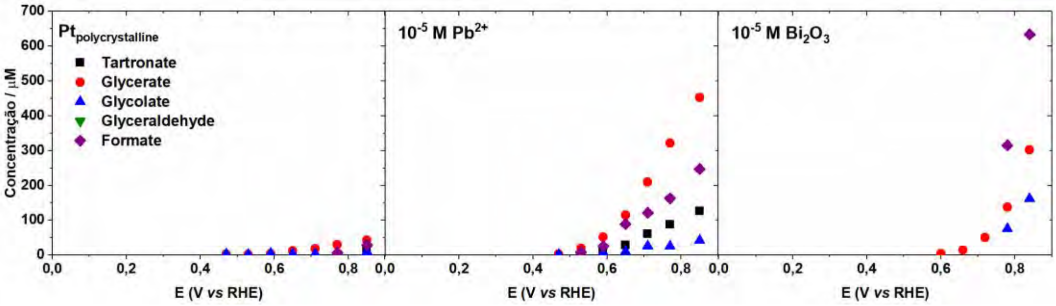

Figure 2: Distribution of the EOG oxidation products with electrode potential for polycrystalline Pt (left), Pb-Pt (center) and Bi-Pt (right) systems. Adapted from (2,3).

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A preliminary study of the electrooxidation of edoxaban

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Edoxaban (EDX) is a novel oral anticoagulant drug, approved by the FDA in 2015 to prevent stroke in atrial fibrillation [1]. EDX act as a competitive inhibitor of factor Xa with higher selectivity compared to thrombin [2]. Here, we present a preliminary study on the electrooxidation of EDX in aqueous media. The voltammograms were recorded using a potentiostat/galvanostat Autolab PGSTAT128 (Ecochemie, Holland) interfaced to a computer and controlled by NOVA 2.1 software. The experiment was carried out in a Britton-Robinson buffer solution using a three-electrode system consisting of a carbon paste electrode (4 mm of diameter) as the working electrode, a Pt wire as the counter electrode, and SCE as the reference electrode. EDX was first dissolved in a mixture of water and acetonitrile (50:50) to prepare a stock solution. Fig. 1 shows the chemical structure of edoxaban and the cyclic voltammograms registered at different concentrations of the drug. The voltammograms show two overlapped peaks in the range of 0.8 - 1.0 V, and another with higher intensity at a more positive potential, about 1.3 V. As they all increased by increasing the concentration of EDX, and no peak was observed by adding only acetonitrile, theses peaks can be attributed to the oxidation process of EDX. The three peaks shifted towards less positive potentials by varying the pH from 5.0 to 10.0 with a visible reduction of the intensity. The effect of the scan rate (25 - 500 mV s^{-1}) was also evaluated. More analyses are being conducted to acquire more information about the electrooxidation process of EDX.

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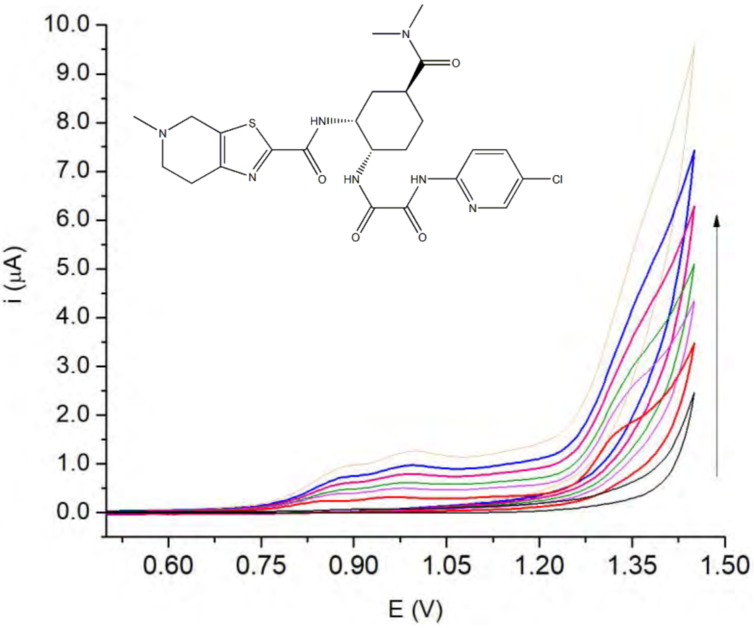

Fig. 1. Cyclic voltammograms at different concentrations of edoxaban obtained in Britton-Robinson buffer solution (pH =6.0) at a scan rate of 50 mV s^{-1}. Arrow indicates concentrations of 0, 10, 20, 30, 40, 50, and 60 μg mL^{-1}.

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Electrodeposition of flower-like and leaf-like gold microstructures on screen-printed carbon electrode

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Gold micro/nanostructures are fascinating due to their wide range of applications in areas including electronics, catalysis, biomedicine, and chemical sensing [1]. Besides their active surface area, they exhibit optical, electronic, and chemical properties that make them promising candidates for the design and fabrication of highly effective electrochemical platforms. There are many synthetic routes to produce different shapes of gold structures [2]. Among the various procedures reported in the literature, electrodeposition is an efficient and convenient method to create gold micro/nanostructures. The size and morphology can be facile controlled by changing the concentration of the gold precursor, the electrolytic solution, the technique, applied potential, and time of experiment [3]. In this work, different gold microstructures were obtained on the surface of screen-printed carbon electrodes (SPCE) by performing constant-potential electrolysis and consecutive cyclic voltammograms. All measurements were performed using a potentiostat/galvanostat Autolab PGSTAT128 (Ecochemie, Holland) interfaced to a computer and controlled by NOVA 2.1 software. The electrolyte solution consisted of a solution of 0.1 M Na_2SO_4 and 30 mM HAuCl4, prepared with ultrapure water (Milli-Q system, 18.2 MΩ cm). Leaf-shaped gold microstructures resulted by carrying out by applying a potential of -0.6V during 600 s. However, different kinds of structures appeared after twenty consecutive cycles of voltammograms registered at 50, 100, and 200 mV s^{-1}. Fig. 1 shows the scanning electron microscopy (SEM) images. These structures significantly increased the electrode surface area of SPCE, as confirmed by comparing the electrochemical response of 1 mM ferricyanide at the electrode surface before and after the electrodeposition.

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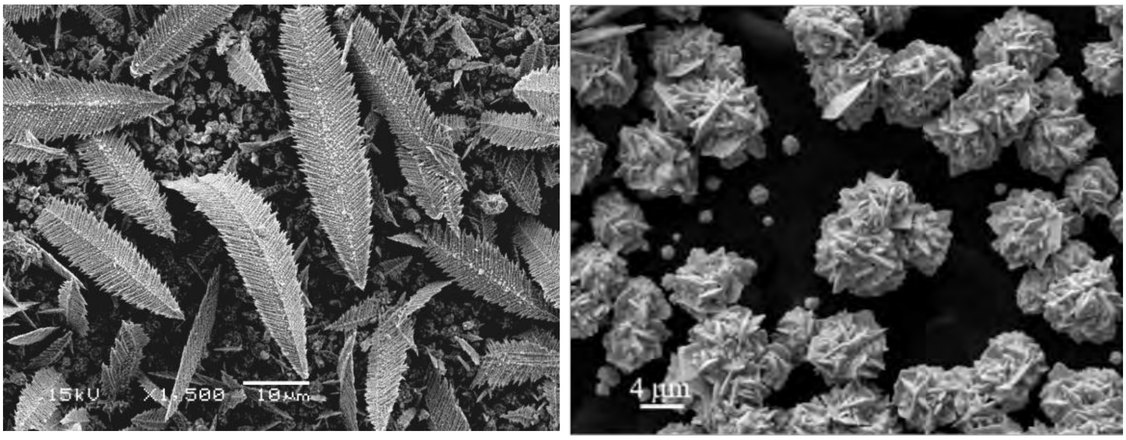

Fig. 1. A) SEM image of the leaf-like gold structures obtained under a constant-potential electrolysis at –0.6V for 600 s. **B**) SEM image of the flower-like gold structures obtained by cyclic voltammetry experiments at 200 mV s^{-1}.

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In-Situ Electrodeposition of Nickel on a Biocathode to Enhance Methane Production from Carbon Dioxide in a Microbial Electrosynthesis System

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Microbial Electrosynthesis Systems (MES) use electricity and microorganisms to produce energy carriers, such as hydrogen (H_2) or methane (CH_4). In what can be called Bioelectrochemical Power-to-Gas (BEP2G) process, MES combines CO_2 sequestration, renewable energy carrier production, and energy storage. In this study, a continuous conversion of CO_2 to CH_4 in a laboratory-scale MES is achieved. The MES cell for CH_4 production was built using Plexiglass plates assembled to create two compartments divided by two layers of electrically insulating Nylon cloth with a total area of 96 cm^2 (anode-cathode interface area). The cathode compartment consisted of a stainless-steel mesh (current collector) and it was filled with 45 g of carbon felt pieces. The anode consisted of a Ti/IrO_2 mesh current collector. The cathode compartment was maintained at a constant temperature of 30°C and continuously supplied with CO_2 and a solution of nutrients. The cathode compartment was initially inoculated with 20 mL of homogenized anaerobic sludge. To further increase the CH_4 production rate, nickel was (*in-situ*) electrodeposited on the cathode carbon felt.

The introduction of Ni at 0.2 g L^{-1} into the influent exhibited a remarkable improvement in CO_2 conversion. At an applied voltage of 2.8 V, the MES with the Ni-modified carbon-felt cathode accomplished a CH_4 production rate of 2.3 L d^{-1}, which was by 30% higher than before Ni was introduced into the influent stream (1.6 L d^{-1}). Similar improvements were noted with other performance parameters, such as the Coulombic efficiency and the energy consumption, which considerably improved from 56% to 73% and 11.5 Wh L_{H2}^{-1} to 7.4 Wh L_{H2}^{-1}, respectively. Furthermore, when the dissolved Ni was removed from the influent solution, the cell performance remained unchanged, suggesting successful *in-situ* electrodeposition of Ni on carbon felt. Electrochemical characterization using the cyclic voltammetry technique confirmed Ni electrodeposition. Overall, the experiment was carried out for over 60 days without observable performance deterioration. In fact, somewhat improved performance was observed with time, likely due to the development of a stable electroactive biofilm. These results demonstrated a great potential of using *in-situ* Ni electrodeposition to improve catalytic properties of the MES biocathode. It can be concluded that bioelectrochemical conversion of CO_2 to CH_4 can be exploited as a potential technology for continuous stable BEP2G conversion combined with CO_2 sequestration.

Can perovskite oxides be used as catalysts for the concomitant production of hydrogen and fine chemicals in electrolyzers?

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The increasing concern about pollution is generating opportunities for bio-based economies. Biomass-derived molecules like glycerol (G) can be utilized as feedstock for the production of value-added chemicals and high purity H_2 in low temperature electrolyzers[1]. In traditional water based electrolyzers the overpotential needed to run the device is high (around 2V), increasing the cost of H_2 production. Once water is substituted at the anode compartment by biomass derivative, the possibility of running the electrolyzer device with smaller overpotential arises as shown in Figure 1. Noble metal-based electrocatalysts are well known for the electrooxidation of small organic molecules, but its high cost and scarcity hinders the application in large scale[2]. Thus, in this work we discuss the possibilities for the application of perovskites oxides (PO) for the electrooxidation of small organic molecules. PO can be synthesized using highly abundant, cheap and non-hazardous materials. Also, they are very versatile due to their compositional (then structural) flexibility[3]. PO have been evaluated for oxygen evolution reaction (OER) with promising results in terms of activity[4]. Considering the oxidation of small alcohols, preliminary studies have shown that PO can oxidize methanol[5], ethanol[6] and glycerol[7] with smaller overpotential than needed for OER. However, the overall performance of these materials with organics are still far from those obtained with noble metals[8]. Thus, systematic studies about the use of PO in anodes for biomass conversion are necessary to link its physicochemical properties with its activity. In this context, fundamental studies involving *in situ* techniques and computational experiments are mandatory to speed up the fundamental knowledge in the field and open the door for the rational development of more active and selective materials.

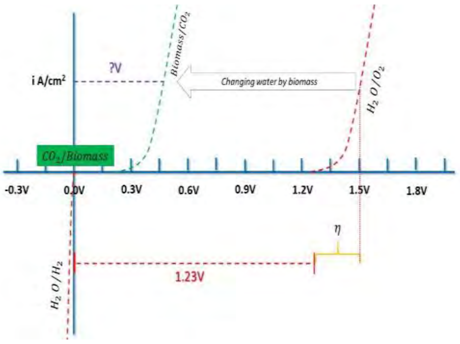

Figure 1: Most important reactions and electrochemical parameters for low temperature electrolyzers. In this method, water oxidation begins at 1.23V and the current follows a Butler-Volmer relationship between current density and potential. The potential at the anode must be equal to 1.23V + η to operate the system at a current of "i A / cm^2." However, with a pricey catalyst like Pt, the hydrogen reaction may be powered close to the reversible potential. Standard potentials for the complete oxidation of several biomass molecules have values around the green rectangle. The difference in potential between the arbitrary I-V curve of the biomass oxidation and the I-V curve of the water oxidation shows that the potential input needed for an electrolyzer is decreased to 1V.

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Long-distance electron transfer by cable bacteria and snorkel for enhanced hydrocarbon degradation in marine sediments

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Degradation of petroleum hydrocarbons (HC) in sediments is often limited by the availability of electron acceptors. Cable bacteria may stimulate the regeneration of sulphate in the anoxic sediment by allowing long-distance electron transport (LDET) to the oxic overlying water, thereby accelerating petroleum HC degradation. Incubations of crude-oil contaminated sediment, showed that cable bacteria accelerate alkanes degradation by +24% compared to control sediment where the growth of cable bacteria was inhibited. Similar degradation rates (+25%) were obtained via the application of graphite snorkels. The combined application of cable bacteria and snorkels yielded the highest rates of HC removal (+46%), and sulphate production via sulphide re-oxidation.

Screening data show that cable bacteria can be common in HC-polluted sediments. Cable bacteria may thus represent key and so far, overlooked players in the self-healing capacity of sediments upon HC spillage, and inspire novel biotechnological approaches for sediment remediation.

Marzocchi, U., Palma, E., Rossetti, S., Aulenta, F., & Scoma, A. (2020). Parallel artificial and biological electric circuits power petroleum decontamination: The case of snorkel and cable bacteria. Water Research, 173, 115520. doi:10.1016/j.watres.2020.115520

Using ion-selective electrodes and mercury microelectrodes: Towards mapping local ion gradients

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The ion and electron transfer processes at interfaces between electrolyte and electrode are of pivotal importance for the overall performance of Li-ion and post-Li batteries. Due to these processes, degradation of the electrode material as well as the electrolyte takes place and an interphase is formed. This solid electrolyte interphase (SEI) at the anode and cathode electrolyte interphase (CEI), respectively, is essential for a stable and safe operation of battery systems such as Li-ion battery and other alkali ion based batteries, since it serves as a protective layer which prevents further decomposition of the electrode and electrolyte while maintaining ionic conductivity. The formation processes of these interphases are not yet fully understood and they are characterized by heterogeneities. Hence, characterization techniques providing spatially resolved information are pivotal to elucidate the heterogenous nature of the interphase as well as the role of the shuttling ion in the formation process. [1]

The combination of a scanning probe microscopy technique such as scanning electrochemical microscopy (SECM) with ion-selective electrodes (ISE), as already shown for biological samples [2,3], or mercury microelectrodes [4] allows the localized and selective detection as well as mapping of ion gradients with high spatial resolution. Due to information on kinetics, ion concentration and substrate reactivity gained from the electrochemical approach and information on local heterogeneity, topographical and morphological changes gained from the scanning probe approach, conclusions on the mechanism of the SEI/CEI formation can be drawn. Next to the fabrication and thorough characterization of micro-ISEs for battery relevant ion sensing as well as mercury microelectrodes for the detection of cations, first SECM measurements at model electrodes will be presented.

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Digital simulation in electrocatalysis, the case of carbon dioxide reduction with diffusion-convection mass transport

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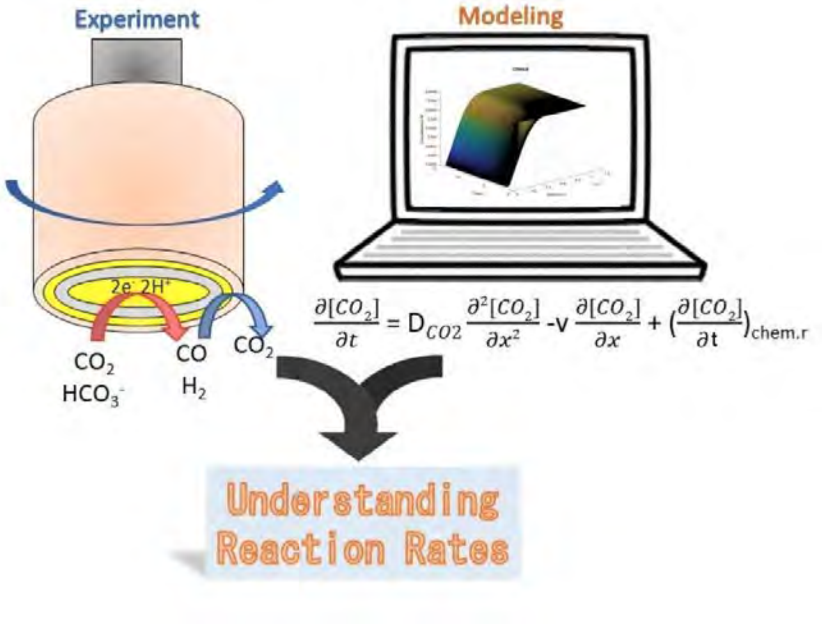
Digital simulation is a powerful tool in electrochemistry to investigate complex systems in which many variables influence the current-potential response, i.e. homogeneous chemical reactions, convection and multiple electron transfers.

The electrochemical reduction of CO_2 (CO_2RR) is complicated by a variety of phenomena, i.e. homogeneous chemical reactions, hydration of CO_2, acid-base equilibria of bicarbonate and carbonate. Moreover, bicarbonate electrolyte has been experimentally proven not only to be a buffer agent, but to actively participate in the electrochemical reaction of CO_2RR, providing CO_2 and to hydrogen evolution reaction (HER) as a proton donor. Thus, understanding the changes in surface concentration of the species is crucial, as they are involved in the equations of the reaction rates.

In this study, we developed a microkinetic model of CO_2 electrochemical reduction of carbon dioxide and hydrogen evolution reaction in bicarbonate electrolyte based on our previous experimental measurements of CO_2RR and HER under well-defined mass transport condition[1].
The surface concentration obtained by microkinetic modelling have been used to calculate the reaction rates of CO_2RR based on different reaction mechanisms. Then, we tested the agreement between the current-potential curves obtained from experiments with the theoretical ones.



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Antibacterial Activity of Silver-Nanoparticle-Based Films Investigated with Scanning Probe Microscopy

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Microbial biofilms are known to exhibit an increased tolerance against biocides and antibiotic treatments in comparison with their planktonic counterparts. Due to their high resilience, biofilms contaminate medical implants and are difficult to eliminate, leading to serious problems for infection controls, increased contaminations and mortality of patients [1]. Novel therapies to prevent biofilm growth, include, among other strategies, coatings containing metal-based nanoparticles (NPs), which are intensively studied [2], in respect to their ability to disrupt biofilms. In presence of silver(I), a stimulation of bacterial respiration is detected with the consequent death of the microbes: this mechanism is also reported in biofilms [3].
In this contribution, silver(I) is studied biocomplateble AgNPs-fluoropolymer (Ag-CF_x) composite films, which were prepared by ion beam sputtering (IBS) deposition [4], are investigated as antimicrobial substrates. The mechanism of the silver(I) release is studied ex-situ by electrothermal atomic absorption spectroscopy (ETAAS) and in-situ by scanning electrochemical microscopy (SECM) in combination with square-wave stripping voltammetry (Fig. 1). In addition, the relation between silver(I) release and the swelling of Ag-CF_x films will be presented, combining electrochemical techniques and atomic force microscopy (AFM).

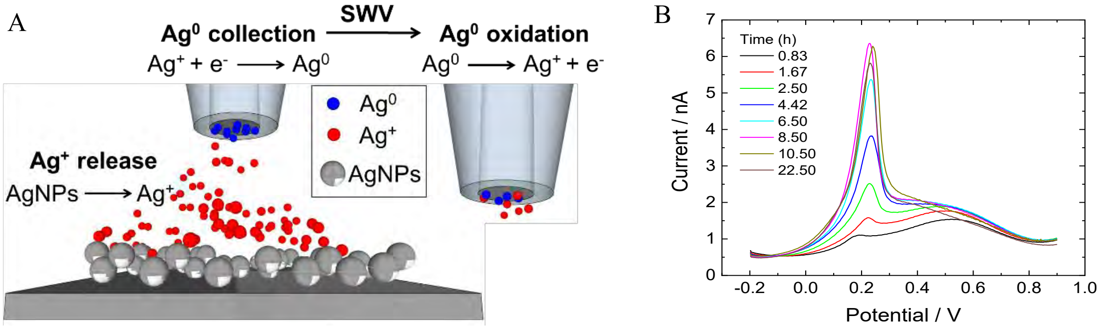

Fig. 1. (A) Scheme of silver(I) release study with SECM-SWV. (B) Square wave voltammograms at different immersion times of Ag-CF_x samples in KNO_3 0.1 M.

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Using iron sulphate to form both pseudo-n-type and p-type liquid thermoelectrics: Non-hazardous and ‘second life’ thermogalvanic cells

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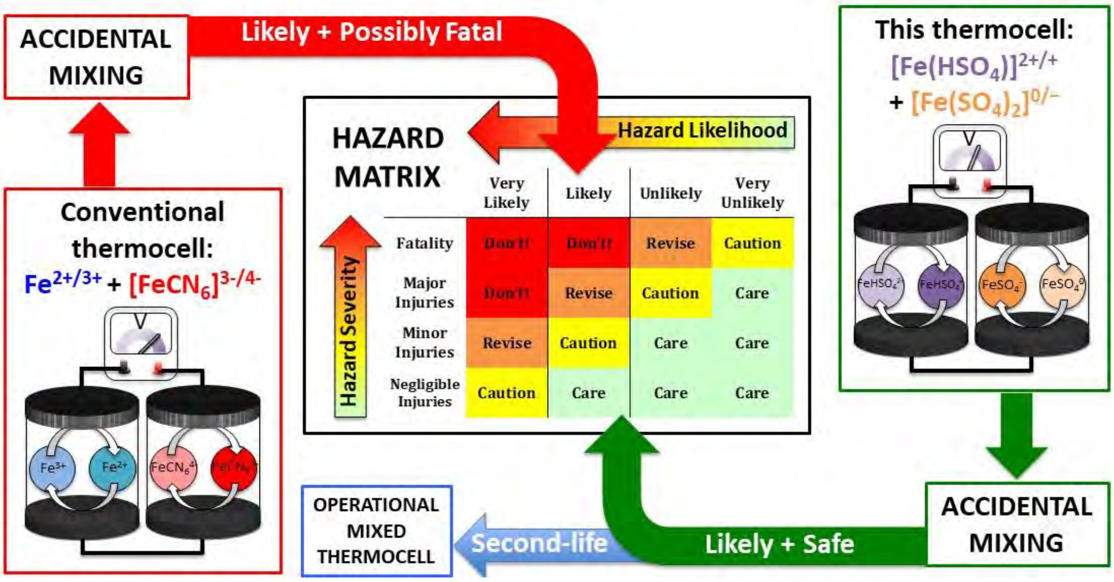
Liquid thermoelectric (or thermogalvanic) cells use a redox-active couple to convert a temperature difference between two electrodes (ΔT) to electricity (ΔV) through the Seebeck effect, where potential difference generated as a function of temperature difference is obserevd as the Seebeck coefficient (Se) where: Se = $\Delta V/\Delta T$. High Seebeck coefficient redox couples such as the acidified $Fe^{2+/3+}$ [1] and $[Fe(CN)_6]^{3-/4-}$ [2] have been fundamentally assessed previously in our group. These systems display Se of *ca.* +1.4 and -1.4 mV K^{-1} (for the $Fe^{2+/3+}$ and $[Fe(CN)_6]^{3-/4-}$ systems respectively), where the positive and negative signs indicate that the hot electrode acts as the cathode or anode respectively.

The main drawback with thermogalvanic cells is the low overall voltage generated from these systems, to overcome this, positive and negative Se systems need to be utilized electrically in series (shown in Fig. 1). To date, the $Fe^{2+/3+}$ and $[Fe(CN)_6]^{3-/4-}$ systems have been typically utilized as combinations of positive and negative Se systems to generate higher voltage devices. However, a combination of the $Fe^{2+/3+}$ and $[Fe(CN)_6]^{3-/4-}$ systems has the potential to evolve high concentrations of toxic HCN. [3] Due to the potential toxicity of the evolved products, a benign combination of positive and negative Se systems needs to be developed to achieve high voltage devices.

Here, we demonstrate that a both positive and negative Se systems have been developed from $Fe(II)SO_4$ and $Fe(III)SO_4$ and an excess of either the $[HSO_4]^-$ or $[SO_4]^{2-}$ ions. Crucially, we also demonstrate that these systems can be mixed safely, where the resulting mixture solution is also found to maintain thermogalvanic activity as a positive Se system that can easily be electrically connected. This demonstrates a single-source, multi-functional thermogalvanic cell that even when mixed maintains thermogalvanic activity, which we coin as a ‘second-life’ thermogalvanic cell, that removes the inherent risk associated with the current state-of-the-art system.



	Very Likely	Likely	Unlikely	Very Unlikely
Fatality	Don't!	Don't!	Revise	Caution
Major Injuries	Don't!	Revise	Caution	Care
Minor Injuries	Revise	Caution	Care	Care
Negligible Injuries	Caution	Care	Care	Care

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Voronoi Diagrams and Diffusion at Random Arrays of Active Sites

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Many practical systems at micro- and nanoscale can be represented as arrays of active sites distributed randomly [1]. As shown previously these systems can be efficiently addressed theoretically by using Voronoi diagrams [2, 3] which allows facile tessellation of the system into the unit cells around each active sites. The overall current flowing in the system can then be evaluated by modelling diffusion-reaction processes inside every unit cell and summing the contributions from individual active sites. Although this approach is tempting by its simplicity and efficiency [3] one should bear in mind that Voronoi diagram representing the unit cells by polygonal prisms remains approximation and as each approximation remains valid only under certain conditions. In this work [4] we show that even for the case of diffusion limited electron transfer (ET) the actual shapes of the unit cells are more complicated and depend on the local configuration of the neighbouring active sites. This was exemplified on the small patches of the random arrays with band-like and disk-like active sites via simulations and in the case of band-like active sites confirmed by analytical derivations.

Importantly, by comparing the total array current obtained by employing Voronoi tessellation and simulation of the system without any approximations we found that they agree well (relative error ca. 5% or less). At the same time, the individual contributions from the active sites are reproduced with a much larger relative error [4]. The latter suggests that in the case of kinetic control or reaction mechanisms that are more complicated than simple ET the diffusion-reaction competition between the active sites may become even stronger eventually leading to significant deviations from the total current predicted on the basis of the Voronoi approximation. This is currently investigated in our team.

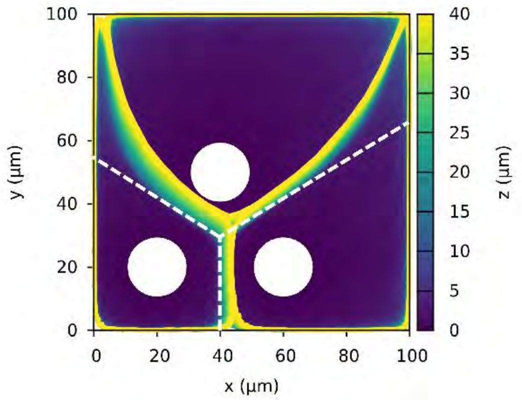

Fig. 1. Comparison between the Voronoi tessellation boundaries (white dashed lines) and the actual boundaries (coloured surface) of the unit cells. Three disk-type active sites are shown as white disks.

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Wastewater treatment and power generation with a scale prototype of a vertical MFC at Universidad Tecnologica de Altamira, Mexico

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Microbial fuel cells (MFCs), which generate electrical energy through a bioelectrogenesis process, are considered one of the most efficient alternative technologies [1]. Two electrochemical processes occur inside the cell: at the anode the oxidation of a biodegradable organic substrate and at the cathode a reduction reaction with oxygen from the ambient, which together lead to current generation and reduction of the organic matter contents. Although considered a promising technology for the generation of electricity, due to the simultaneous generation and wastewater treatment [2], there is the need of process characterization to overcome the limitations encountered during scaling up [3]. This work presents the study of the process variables of a MFC prototype built with low-cost and recycled materials. Three 1 L MFCs were built and installed at UTA, using domestic wastewater as substrate, graphite felt cathode, and electrocatalyst obtained from recycled anodes from alkaline batteries; graphite felt anode; proton exchange membrane of treated wood and external electrical resistance of 500 Ω as shown in Fig. 1. The cells were instrumented to measure voltage, internal reactor temperatures, ambient temperature and relative humidity. Conductivity, pH, salinity, and TDS were measured on a HACH multiparameter and chemical oxygen demand (COD) with a Hanna Instruments photometer. In the first 100 hours a 72% decrease in COD and 74% decrease of pH in 3 MFCs was observed due to the metabolic activity of bacteria (Fig. 2,3). After 100 hours of acclimatization, the best performing cell (MFC3) started with recharging of new substrate. The voltage evolution during the 180-hour operation is shown in Fig 4. As conclusion, oxidation and reduction reaction exist and maximum electrical values were 0.298 V and 0.59 mA. This characterization of the factors that affect the cell will establish the bases for the construction of a wastewater treatment plant in this University.

Fig 1. Setup of MFCs

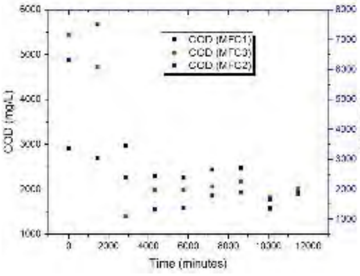

Fig 2. COD evolution

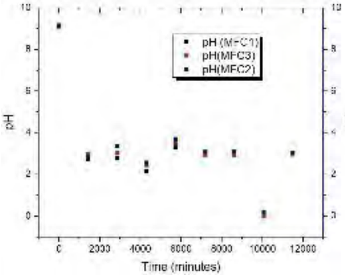

Fig 3. pH vs time of MFC-3

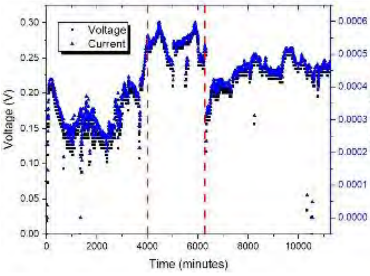

Fig 4. Voltage evolution

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Synthesis of Stable Polyfluorinated Anion Exchange Membrane by Chemical Modification of Aquivion®

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Finding new ways for sustainable energy production and storage has been the object of intense research over last decade. In this context, Fuel Cells (FCs) have attracted much attention thanks to the use of hydrogen, which is retained to be the energy vector of the future. Commercial low temperature FCs are based on a Proton Exchange Membrane (PEM), such as Nafion®. However, the high cost of these devices, chiefly due to the use of Platinum Metal Group elements as electrocatalysts (ECs), prevents their large-scale application. Anion Exchange Membranes (AEMs) are largely investigated because the use of an alkaline pH environment opens the possibility to exploit cheaper ECs based on Fe, Ni, Ag [1]. Moreover, the alkaline environment facilitates the Oxygen Reduction Reaction at the cathode with respect to PEM working conditions [2].

Here we present a synthetic strategy to convert commercial protonic membranes into AEM. In particular, the polyfluorinated PEM Aquivion® EW=980 g/mol (Solvay) is functionalized by reaction with aqueous diamine solution to obtain sulfonamide AEM (see insert of Fig. 1). This allows to maintain the same mechanical and chemical resistance of the pristine membrane but at the same time, it increases the thermal stability thanks to the formation of sulfonamide bonds. This functionalization is carried out in an aqueous media, which is clearly advantageous from the environmental point of view. The in-plane conductivity is 1,1*10^{-1} Scm^{-1} at 80°C and with relative humidity 100%.

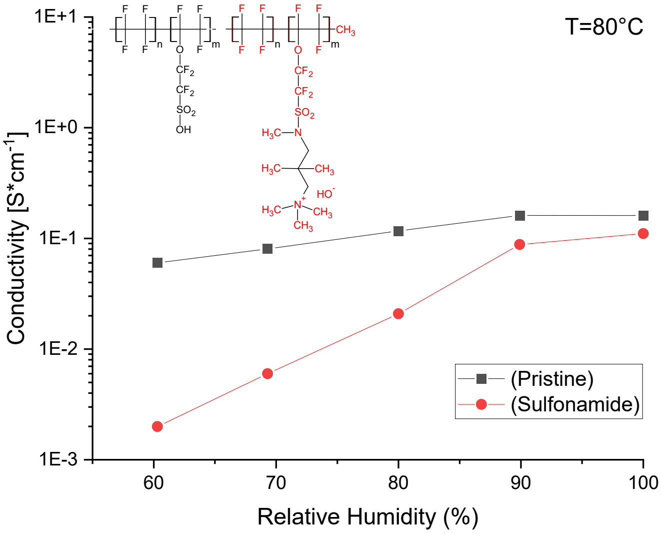

Fig. 1 - Conductivity measured as a function of the Relative Humidity for the Pristine (black) and the Sulfonamide (red) Aquivion® at 80°C. The inset shows the polymer structure of PEM (left) and AEM (right) Aquivion®.

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Validation of a two-dimensional model for vanadium redox-flow batteries

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Redox-flow batteries (RFBs) can play a crucial role in the future electricity supply to balance the time lag between the generation of electrical energy from photovoltaics or wind power and the demand for electrical energy. However, to deploy the technology on a large scale, significant cost reductions are required. For this task, a thorough understanding of the reactions and processes taking place within a redox-flow battery is crucial and this knowledge can be significantly improved by using a suitable mathematical model to describe the processes in a single cell of an RFB. However, the available mass transport correlations result in Sherwood numbers which vary over two orders of magnitude [1-5] and therefore significantly affect the accuracy of the model.

In this work the validation of a two-dimensional model for the prediction of polarization curves of an RFB is presented, focusing on the refinement of the mass transport correlation. Newly developed potential probes are used for in-situ measurements of solid and liquid phase potentials within a vanadium RFB [6, 7]. Combined with systematic variation of flow rate and state of charge, the experiments build a robust data base. After parameter estimation, the model predictions are in good agreement with the experimental data (exemplary shown in Fig 1 A). The resulting mass transport correlation is well in line with the most appropriate literature data (Fig. 1 B). Using the improved correlation, the RFB model provides more accurate predictions and better support for optimizing the cell design.

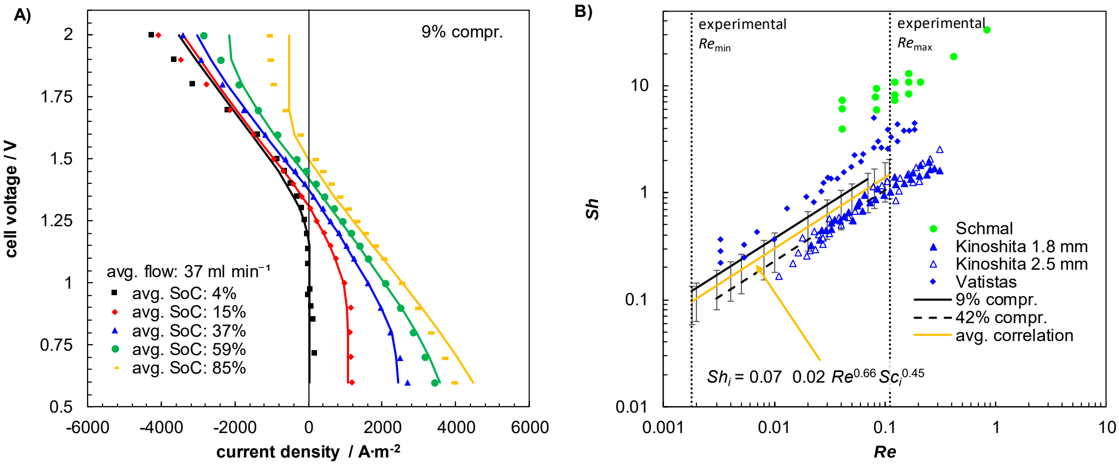

Figure 1: A) Exemplary polarization curves of a 100 cm² cell setup with GFD4.6A carbon felt and Nafion® 117 membrane for low (left) and high (right) flow rate. Flow rate and state of charge of each half-cell electrolyte are given within the figure. Compression rate of the carbon felt is 9%. Points represent experimental data, lines indicate simulations. B) Dimensionless Sherwood correlations from literature compared to results from model-based parameter estimation.

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Long term oxygen sensing in 3D hydrogel scaffold cell cultures

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The launch of a new drug is an extremely long and expensive process, lasting from 7 to 15 years with costs exceeding $1400 mln per drug[1]. The process includes: basic research; *in vitro* (with 2D cell cultures) and *in vivo* (using animals) preclinical research and in the end clinical trials. Animal models are controversial not only because of the ethical aspects, but also because of their imperfect reflection of the human body, which results in over 30% drugs withdrawals during the clinical trial phase[2].

Three dimensional cultures are an alternative providing a better understanding of complex cell–cell interactions. In contrary to simple monolayer cultures, they allow cell growth in all directions as well as secretion of signaling molecules and specific proteins in normal levels as in the human body[3]. Among many culture systems, hydrogels are the most promising platforms for cell cultures due to their transparency, good diffusion of nutrients and similarity to many soft tissues[4]. While traditional analysis is mostly based on optical methods including broadly understood microscopy techniques and measurements of fluorescence, analysis in 3D requires more advanced and expensive techniques in order to reach deep structures. This is the main reason why 3D cell cultures have not yet achieved wide implementation despite their obvious advantages over 2D cultures and more than 50 years of research. However, using electrochemistry, we are able to do real-time analysis *in vitro.* Oxygen and glucose consumption measurements provide us with a lot of information about cell viability and can be translated to toxicity during tests of new drugs.

For such systems electrodes need to withstand prolonged (at least 3-4 weeks) contact with the cell culture matrix and the surrounding medium, thus biofouling is a major issue. That is why we have tested major antifouling layers including: polymers (e.g. Nafion®, phenylenediamine, polyvinyl chloride, polysilicate matrix), hydrogels (e.g. polyhydroxyethyl methacrylate), protein (e.g. albumin), polyethylene glycol and poly-L-lactic acid. Electrodes were first coated with syringaldazine, which is easily adsorbed on carbon surfaces and provides an easy to interpret response towards pH changes[5]. It is also very stable in buffer solutions but quickly desorbs in more complex media, thus making it an excellent probe for measurement of beneficial impact of antifouling layers. Tests were first conducted on macro- glassy carbon electrodes and later on low-cost pencil based sensors (250 μm diameter) as it was shown that some layers are less stable due to the big size of the electrode surface. It was revelated that polysilicate matrix, poly-L-lactic acid, polyhydroxyethyl methacrylate are suitable candidates for antifouling layers for electrochemical sensors.

At the same time we conducted experiments directed at possibilities of oxygen sensing in hydrogels at various potentials. Initial experiments revealed that 2,9-dimethyl-1,10-phenanthroline as well as a porphyrin complexes with cobalt effectively reduce the potential value for oxygen sensing as compared with Nafion® coated sensors, in both acidic and neutral pH. While in PBS results are immediate, measurement in hydrogels results in the answer extended in time, indicating diffusion problems. Current measurements include oxygen sensing not only in hydrogels and cell culture medium but also with growing cells.

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Application of a Schiff base derivative denatured cytochrome c analogue, for the analytical reporting of nitric oxide.

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Biointergrated sensors involve the biological electron transport between proteins and polymeric materials. Immobilization of biomolecules often compromise the activity of the enzyme. Losses have been attributed to conformational changes or interactions between the biomolecule and the solid surface. Investigations into the redox behaviour of cytochrome c revealed compromised electron transfer to metal surfaces as result of adsorption denaturation[24]. Modification of electrode surfaces by chemisorbed self-assembled monolayers (SAM) resolved this limitation. NO has been reported to coordinate strongly with the iron heme of cytochrome c to form linear nitrosyls with the Fe^{2+} metal centres. Coordination of nitric oxide to the iron centres are expected to alter the redox behaviour of the system. However, nitric oxide has been reported to exhibit trans-effects which would inhibit coordination to the iron centre. Similar findings were recorded in study to reproduce the electrochemistry of denatured cytochrome C. The poor electrochemical response of the denatured cytochrome c metal centre to nitric oxide was attributed to steric crowding surrounding the heme.

In this work, a novel Schiff base was synthesized by cross-linking naphthalene to pyrrole to produce the monomer, N,N-bis((1H-pyrrol-2-yl)methylene)naphthalene-2,3-diamine), by simple reflux chemistry. The structural analysis of the ligand-Fe complex indicated a square planar co-ordination that presented Fe in a favourable position for NO co-ordination.

A novel Schiff base was synthesized by cross-linking naphthalene to pyrrole to produce the monomer, N,N-bis((1H-pyrrol-2-yl)methylene)naphthalene-2,3-diamine). The iron ligand complex was electrodeposited onto screen printed carbon electrodes (SPCE) for electrochemical evaluation, over the potential window of -1 V and 1 V vs Ag/AgCl. The sensor demonstrated electrochemical properties analogous to that of the denatured cytochrome c system. The response of the sensor towards NO generated in situ from the NO donor, diazeniumdiolates (Z)-1-(N,N-diethylamino)-diazen-1-ium-1,2-diolate (DEANONOate), which spontaneously decomposes to nitric oxide in neutral pH. The quantitative analysis of NO was evaluated by spectroscopic and electrochemical methods, with very promising results.

Electrochemical and Physico-Chemical Properties of the Separation Materials for Lithium-Ion Batteries on the Basis of Electrospun PVDF|PTFE, PP and Glass Fibers

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Nanofibers materials produced by electrospinning method can be applied as separators in lithium-ion batteries. This method of synthesis is characterized by simplicity of hardware design, high energy efficiency and variability of conditions. The separation material based on polyvinylidene fluoride (PVDF) and its copolymer with polytetrafluoroethylene (PTFE) was obtained by capillary-less electrospinning [1]. In the present work the optimal synthesis conditions were established. The average fiber diameter was determined in the range of 100-250 nm by scanning electron microscopy (MIRA LMU Tescan) (Figure 1a). The bulk porosity of the obtained material was 71.43%, thickness 50 µm, surface density 27 $g \cdot m^{-2}$, wettability by electrolyte 800%. We studied the electrochemical behavior of a $Li_4Ti_5O_{12}$ electrode in half cells with a metallic Li counter electrode and 0.67 M $LiClO_4$ electrolyte in a mixture of propylene carbonate (PC) and dimethoxyethane (DME) (7:3), and three types of separators: based on electrospun PVDF|PTFE, commercial polypropylene (PP) and glass fibers (GF).

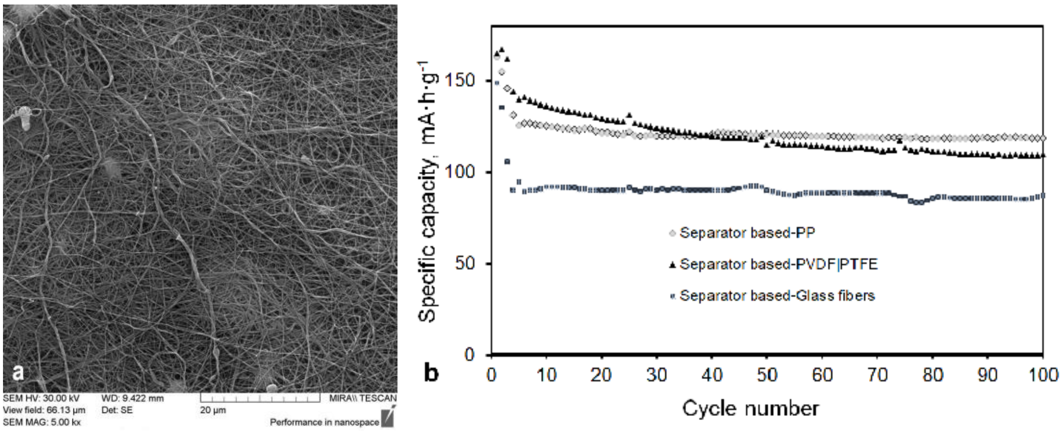

Figure 1. SEM micrographs of the PVDF|PTFE-based separator (a) and galvanostatic discharge capacity of the $Li_4Ti_5O_{12}$ electrode with electrospun PVDF|PTFE-based separator as well as conventional PP-based and GF-based separators at cycling under the specific current in the range of 0.1C – 0.5C during first three cycles and under 1C current during subsequent 100 cycles (b).

The galvanostatic charge-discharge cycling of the cells was carried out in the following range of currents: from 0.1 C to 1 C during the first four cycles and then at 1 C current up to 100 cycles. Cells with the electrospun PVDF|PTFE separator demonstrated higher C-rates with respect to the cells with conventional separators based on PP and GF: at equal currents, higher capacity values of the $Li_4Ti_5O_{12}$ electrode during long-term cycling were observed.

A decrease in the working electrode polarization and an increase in the cycling capacity in the case of the electrospun separator in comparison with the conventional separators based on PP and GF were established. The state of the electrodes and the separator in the cell was monitored by electrochemical impedance spectroscopy (EIS) method. The parameters of the electric equivalent circuit and the diffusion coefficient of lithium ions in the $Li_4Ti_5O_{12}$ electrode for the cells with each type of separator were determined and compared.

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Formation of Mn-substituted $Na_{1+2x}Mn_xTi_{1-x}(PO_4)_3$ (x = 0.0 – 1.5) from Density Functional Theoretical and Cluster Expansion Analysis

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The development of novel rechargeable batteries is currently one of the most important topics in science and technology. Although Li-ion batteries are becoming the leading technology, they face a number of problems like safety and rare and expensive (Co, Li, Ni) raw materials needed for production. Na-ion batteries might be based on inexpensive and widespread materials and could be a viable alternative in applications where particularly high energy densities are not required [1]. Natrium SuperIonic Conductor (NASICON) framework compounds are attracting a lot of attention as potential electrodes from the battery research community [2]. Mn-based NASICONs are deemed as very suitable high voltage positive electrode materials for Na-ion batteries [3]. In this work, a part of the Na-Mn-Ti-PO4 phase diagram corresponding to Mn-poor and Mn-rich solid solutions of different concentrations in the NTP-123 system $Na_{(1+2x)}Mn_xTi_{(2-x)}(PO_4)_3$ $\{0 \leq x \leq 1.5\}$ was constructed using the Cluster Expansion approach and periodic density functional theory calculations [3]. Results indicate a limited thermodynamic stability window at around x = 1.0, which might provide valuable guidance for the experimental effort to prepare various Mn-substituted NASICON compounds (Fig. 1).

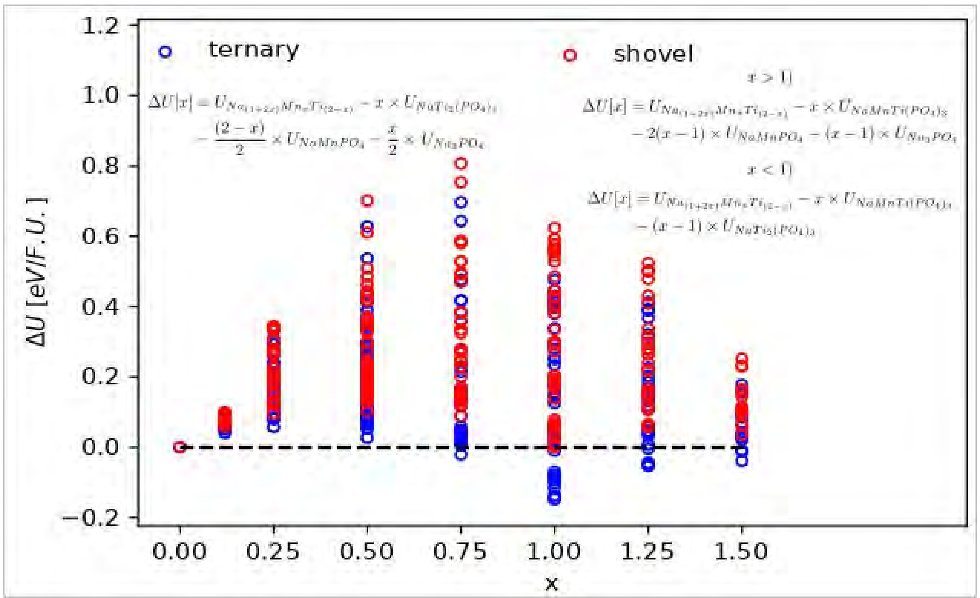

Fig. 1. Formation energy diagram. The case where x=1.0 is used as a reference point is marked in red.

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Synthesis and Electrochemical Properties of the Electrode Materials on the Basis of $Li_2Fe_xMn_{(1-x)}SiO_4$ and $Li_4Ti_5O_{12}$ for Lithium-ion Battery

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Modern li-ion batteries based on $LiCoO_2$/graphite and $LiFePO_4$/graphite electrochemical systems offer customers a choice of high energy density or safety at operation. In the present work, we considered the alternative of li-ion system based on $Li_4Ti_5O_{12}$ (LTO) / $Li_2Fe_xMn_{(1-x)}SiO_4$ (LFMS).

$Li_4Ti_5O_{12}$ was obtained by the solid-state synthetic rout with preliminary mechanical activation. At the first stage, the Li_2CO_3 and TiO_2 mixture was subjected to mechanical activation. Next step was an annealing at 750°C for 5 hours in an air atmosphere.

$Li_2Fe_xMn_{(1-x)}SiO_4$ ($x = 0.33$) was obtained by sol-gel method. At the first stage, the initial precursors ($LiOH \cdot H_2O$, $Fe_2C_2O_4 \cdot 2H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, ethylene glycol, tetraethoxysilane) were mixed until a sol was formed. Then the sol was evaporated to form a gel. This gel was subjected to heat treatment at a temperature of 650°C for 5 hours in an argon atmosphere.

The electrochemical properties of both anode and cathode materials were studied by galvanostatic charge-discharge cycling. We used three-electrode laboratory cells with lithium reference and auxiliary electrodes to support the work of the electrode under investigation. A 0.67 M solution of lithium chlorate(VII) $LiClO_4$ in a mixture of propylene carbonate and 1,2-dimethoxyethane with a volume ratio of 7:3 was used as an electrolyte. The galvanostatic charge-discharge cycling of the cells was carried out at the rate of 0.02C-0.1C in the potential range of 1.50–4.50 V (vs. Li) for LFMS, and at 0.2 C in the potential range of 1.00–2.50 V for LTO using a P20X8 multichannel potentiostat-galvanostat (Elins, Russia).

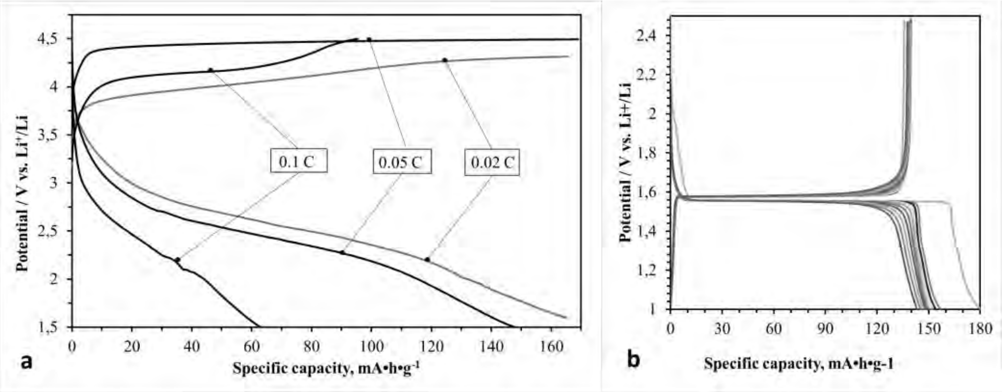

Figure 1. Galvanostatic charge and discharge curves of $Li_2Fe_xMn_{(1-x)}SiO_4$ ($x = 0.33$) electrode at the rate of 0.02 C – 0.1 C (a) and $Li_4Ti_5O_{12}$ electrode (b) at the rate of 0.2 C.

LFMS electrode showed increasing of specific capacity up to 164 $mAh \cdot g^{-1}$ (Figure 1) at 0.02 C rate comparing to usual specific capacity of Li_2FeSiO_4 electrode [1]. The shape of charge and discharge curves of $Li_2Fe_{0.33}Mn_{0.67}SiO_4$ electrode is smoother than Li_2FeSiO_4 electrode, and potential hysteresis between curves is lower.

LTO-based electrode material showed specific capacity of 140 $mAh \cdot g^{-1}$. The shape of the curves is identical for LTO obtained by other authors [2] and is characterized by a potentiostatic plateau at 1.55 V.

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The effect of microstructure on overall and local corrosion and passivity behaviour of high strength steels

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High-strength steels are widely used in many applications including oil and gas production, transportation and infrastructure, as a result of their optimised mechanical properties, relatively low price and high availability. However, most low-alloy steels are susceptible to corrosion. Corrosion of steels has significant negative consequences for the economy, the environment and human safety. The microstructure of the steel alloys is one of the factors influencing their corrosion resistance. It is desired to optimise the microstructure design of the alloy to control or enhance the corrosion resistance. For this, more insight into the interaction between microstructure and corrosion is needed. The influence of microstructural features on the corrosion and passivity of the steels is not well understood, with occasional contradictory tendencies. This is due the complexity of the microstructure where many different features (grain size, phase, crystallographic orientation, dislocation density) play a role in the overall corrosion and passivity behaviour. To separate the sole effect of microstructural features, it is crucial to design well-controlled model alloys by heat-treatments or thermomechanical processes to limit the combined effects of microstructural features on passivity and corrosion behavior.

In this work, a study is presented in which the individual effect of grain size and microstructural defects (e.g. dislocation density, grain boundaries) on the passivity and corrosion behaviour of model alloys is investigated. Three aspects are considered. (1) The role of grain size on the passive layer of pure iron is investigated with model alloys with grain sizes between 25 and 91 μm. It was observed that grain refinement leads to increase in the passivity current density in the potentiodynamic polarization curves and lower resistance in the electrochemical impedance spectroscopy (EIS) measurements. This effect in barrier properties of the passive film stems from the increase in donor density measured with Mott-Schottky analysis and decrease in fractions of protective γ-Fe_2O_3 in the passive film (composed of Fe_3O_4, γ-Fe_2O_3 and $FeO(OH)$) that it is measured with X-ray photoelectron spectroscopy (XPS). (2) The effect of dislocation density on the corrosion behaviour of interstitial free (IF) ferritic steels was investigated in 0.1M HCl solution. It is shown that the corrosion rate increases with increase in dislocation density. This is attributed to the increasing Volta-potential difference in between grains with increase dislocation density, measured by Scanning Kelvin Probe Force Microscopy (SKPFM). This leads to a higher driving force for galvanic coupling. (3) In the third case, the role of microstructural defects (dislocation density and grain boundary) on passive layer properties of IF steels is studied. It is revealed that the barrier properties of passive film deteriorate with increasing microstructural defect density due to an increase in donor density and a lower γ-Fe_2O_3 fraction in the passive film.

Electrochemical Analysis of Fentanyl and Fentanyl Analogs Towards a Rapid Screening Assay

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The use of opioids is on the rise nationwide, and the potential danger of an unintentional exposure is increasing. One of the current deadliest synthetic opioids if fentanyl. There are also numerous fentanyl analogs that have been synthesized, often illicitly, that are hazardous: some of which are more potent than fentanyl itself. There are many laboratory-based methods used to detect fentanyl, but they lack the portability and rapid response necessary for early detection in the field. The focus of this project is to use electrochemistry as a fast detection method answering those needs and allowing for early detection of fentanyl and fentanyl analogs. In the body, fentanyl undergoes an oxidative N-dealkylation reaction, which generates metabolites. The electrochemical reaction of fentanyl appears to be mimicking this, with an irreversible oxidation, which then generates metabolites in solution. We use cyclic voltammetry to monitor oxidation of fentanyl and the oxidation and reduction of possible fentanyl metabolites. The irreversible oxidation peak appears around 0.80 V *vs.* Ag/AgCl for fentanyl, and this irreversible oxidation results in additional oxidation and reduction peaks observed in subsequent scans. The parameters to electrochemically characterize fentanyl are currently being optimized, such as the supporting electrolyte, concentration of the supporting electrolyte, working electrode, and scan rate. Square wave voltammetry (SWV) is also being considered to analyze the oxidation of fentanyl, because of the greater sensitivity of the method. The optimal parameters for the step, amplitude and frequency are being explored for SWV. The long term goal of this project is to develop a method common to fentanyl and fentanyl analogs to allow for a rapid detection of these drugs that will benefit in-field techniques.

Electrochemical Tape-and-paper-based Chlorate Sensors for Forensic Applications

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The use of chlorate salts as oxidizers in improvised explosives devices (IEDs) has recently increased. IEDs are a global threat due to easy access to raw materials, many manufacturing instructions available on the internet and their lethal potential. The standard methods to detect chlorate are mostly designed for laboratory testing and thus do not meet the requirements for in-field detection. Recent developments in electroanalytical assays integrated with flexible substrates have led to user-friendly analytical devices which are inexpensive, portable and disposable. We are developing an electrochemical tape-and-paper-based device for rapid in-field detection of traces of chlorate. The sensing element of our device is an electrodeposited molybdate layer. Indeed, chlorate was reported to have a catalytic effect on the reduction of molybdate. Our sensor detects chlorate by monitoring the change in redox activity of the electrodeposited molybdate using cyclic voltammetry and other electrochemical techniques. We have effectively demonstrated the detection of chlorate in solution and started evaluating the quantification capabilities of the device. We optimized the conditions for the electrodeposition of molybdate (supporting electrolyte, scan rate, pH, type of acid, concentration of molybdate, etc.) by cyclic voltammetry. In addition, we are evaluating square wave voltammetry and differential pulse voltammetry to achieve the most observable effect of chlorate on the molybdate sensing layer. Also, a quality control of the sensors has been developed through chemometric methods. In order to allow a convenient sample collection at crime scenes, an in-field presumptive test, and storage and transport for in-laboratory confirmatory tests we are optimizing the design of tape-encased prototypes. The sensing element of the tape-and-paper-based device is sandwiched in a wider layer of tape which will protect the electrodes from damage when collecting samples in-field. This research was made possible with the support of the National Institute of Justice (2017-DN-BX-0172).

Fabrication and Deposition of Metallic Nanoparticles By Plasma Electrochemistry In Ionic Liquids

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Metal nanoparticles have found extensive attention due to their unique electronic properties, chemical reactivity and potential applications such as: catalysis, optical, magnetic and electronic devices.

Ionic liquids are well known in today's literature to be successfully employed for the synthesis and stabilization of metal nanoparticles without the addition of stabilizing agents. Moreover, ionic liquids have very low vapor pressures (typically 10^{-9} Pa at room temperature), which makes them suitable in either vacuum or atmospheric pressure experiments as fluid substrates or solvents.

Plasma electrolysis, is carried out to produce metallic, alloys or ceramic nanoparticles. Unlike conventional electrochemistry system, in plasma electrolysis system, the cathode or the anode is positioned just above the electrolyte surface, and the counter-electrode is immersed in the electrolyte. For the fabrication of metallic nanoparticles, plasma-induced cathodic discharge electrolysis technique is used. In principle, the cathode is positioned just above the electrolyte surface, and a plasma-induced stationary discharge is generated between the cathode and the electrolyte surface to allow for continuous electrolysis. The discharge is maintained by electron emission from the cathode, whereby atmospheric argon gas is partially dissociated to form condensed plasma in the gas phase. Therefore, when the metal ion source is dissolved in the ionic liquid, fine metal particles are formed on the surface of the ionic-liquid, which sizes are in the nano- up to micro-meter scale (depend on the experimental conditions). The plasma–electrolyte interface can provide a reactive region where active species are formed; further, due to the high-energy electrons in the plasma region, plasma chemistry and electrochemistry reactions occurs, which deviate from the conventional Faraday Law. Ionic liquids are well suitable electrolytes for the plasma electrochemical processes, because compared to water it is much easier to obtain stable and homogeneous plasma, due to their low vapor pressure.

In this work, we will demonstrate plasma electrochemistry capabilities to fabricate metallic copper nanoparticles using $CuSO_4$ salt which is dissolved in1-Ethyl-3-methylimidazolium ethyl sulfate ([EMIM][$EtSO_4$]). Glow plasma was formed in the cathode-electrolyte interface, under atmospheric pressure conditions using argon gas flow which was continuous supplied above the solution. We used a DC power source to apply 200V of potential difference, between the cathode (tungsten wire) and copper foil anode. Our visual pictures of the cell clearly show formation of particles that diffuse from the surface to the bulk electrolyte. Our current vs. time data, combined with in-situ optical emission spectroscopy, allow us to recognize a pattern of particle nucleation followed by growth of the nanoparticles in the ionic liquid bulk. Initial experiments were conducted to obtain Cu nanoparticles-coated carbon paper electrodes. We also extracted nanoparticles from the ionic liquid solution for further elemental analysis such as XRD and TEM. Since electrolysis using multi-discharge electrodes array can be achieved, it seems in the present research stage that plasma electrolysis method is suitable for the mass production of a variety of nanoparticles, whether discrete or incorporated in substrates.

Modification of carbonaceous nanostructured materials for application in Li-Ion batteries

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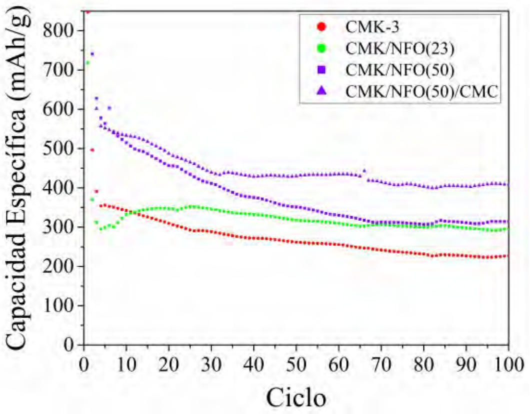
Li-Ion batteries (LIB) have been exhaustively studied because of their potentialities for green transportation and renewable energy storage due to their high power, high energy density and long cycle life [1, 2]. Most commercialized LIB employ graphite as the principal material for the anode, however this material has a low theoretical capacity. Consequently, a wide range of materials has been considered to replace or modify it in order to increase the capacity of the anodes [3]. On the other hand, it was shown that the use of carbonaceous highly ordered two-dimensional porous material CMK-3 as anodes in LIB leads to a significant increase in the conduction of lithium-ion and electrons [4]. In this work, we present a new material based on CMK-3, functionalized by NiFe2O4 spinel, using different impregnation methods. The employment of this particular spinel is grounded on his promising features, for e.g. it has a high theoretical capacity, and both Ni and Fe are low-cost abundant elements (which is important for the possible applicability to the industry) [5].

The resulting materials were characterized by means of the following techniques: Low and high angle x-ray diffraction (DRX), scanning and transmission electron microscopy (SEM and TEM), elemental analysis (EDX), nitrogen adsorption isothermal analysis with BET model, ultraviolet-Visible diffuse reflectance spectroscopy (UV-vis), programmed temperature reduction (TPR), X-Ray emitted photoelectron spectroscopy (XPS).

The following graph shows the battery performance by means of galvanostatic cycling considering different variables: impregnation method (wet and dry), percentage of spinel (23% y 50%) and the binder type (PVDF y CMC).



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Nickel (II) atomically dispersed in carbon nitride improving TiO_2 behavior as photoanode

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In contrast to observed in conventional methods, like the steam methane reforming, H_2 molecule can be satisfactorily generated by electrochemical and photoelectrochemical (PEC) methods. The main advantages in methanol oxidation reaction (MOR) is the possibility to obtain H_2 by a greener method (without large CO_2 emissions in comparison to fossil fuel consumption) [1]. The use of TiO_2 in photo assisted MOR, especially as composites or heterojunctions, using materials of high charge mobility, like graphene, carbon nanotubes, and poly (heptazine imide) (PHI) can reach high yields. PHI structure is up to date one of the closest structures from a "truly graphitic" carbon nitride. Obtained from relative low-cost precursors [2], PHI shows a suitable band gap for utilization of visible radiation (around 2.7 eV), and also can be used to stabilize transition metals as single sites in its structure, proportioning the maximum utilization of the element, in comparison to nanoparticles or clusters [3]. In the present work, we report the synthesis and application in MOR of a photoanode based on TiO_2 loaded with PHI(Ni) (PHI structure containing nickel II atomically dispersed). For the synthesis, the TiO_2 paste was loaded with 2.5 % wt. of PHI and PHI(Ni), spin coated in clean FTO electrodes at 3000 rpm for 30 seconds, obtaining initially a thin film (95 nm thickness), that was thermal annealed at 400 ºC for 20 min in air. The photoelectrochemical experiments were conducted under UV light (365 nm, $100 mWcm^{-2}$) using acidic solution (0.5 mol L^{-1} H_2SO_4) and methanol 13.8 mol L^{-1}. The bare TiO_2 film produced achieved a photocurrent of 109 $\mu A\ cm^{-2}$ at 0.2 V vs. RHE. On the other hand, a significant increase in the activity was observed for the photoanodes containing carbon nitride (pure and containing Ni^{2+} single atoms), TiO_2-PHI and TiO_2-PHI(Ni) films reached 185 and 441 $\mu A\ cm^{-2}$ at the same potential, respectively. The better activity can be explained by two factors: (i) the formation of a TiO_2/PHI heterojunction that leads to better charge separation, and (ii) Synergism between the heterojunction along with the cocatalysis of MOR by $Ni^{2+}|Ni^{3+}$ species that facilitate the charge transfer process. As the TiO_2-PHI(Ni) film proved to be the most promising, it was studied the influence of the thickness of the film, repeating the deposition process. The 30-layers deposited TiO_2-PHI(Ni) film reached a photocurrent of 11 mA cm^{-2} in 0.2 V vs RHE, the best MOR photoelectrochemical activity of films with higher numbers of layers is directly related to the material's absorptivity. While the one-layer TiO_2-PHI(Ni) film was almost translucent and, the 30 layers on the other way had a high opacity. Also, the excellent stability of this film must to be emphasized, the initial photocurrent decays only a 5% at 120 min of measurement, Lastly, *in situ* FTIR measurements allows insights about the reaction mechanism, the three samples TiO_2, TiO_2-PHI and TiO_2-PHI(Ni) apparently follows the same pathway of oxidizing methanol to formaldehyde in dark, and in the UV irradiation higher oxidized products as formic acid and CO_2 are obtained.

Acknowledgements

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A multivariate exploratory analysis applied to a simultaneous voltammetric determination of dopamine, ascorbic acid and uric acid

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Electrochemical techniques offer the advantages of simplicity, low cost, and quickness for analytical determination of several biomolecules, including dopamine (DA), ascorbic acid (AA) and uric acid (UA). However, due to their very close oxidation potential, to perform a simultaneous determination of these analytes usually requires the use of non-conventional electrodes, capable of producing well-defined and separated oxidation peaks. In this case, the use of mathematical procedures for pattern recognition on multivariate data analysis offers a great perspective to solve the drawback of overlapping peaks [1,2]. This work shows an exploratory study of analysis by hierarchical clusters (HCA) and principal component analysis (PCA) in the simultaneous determination of DA, AA, and UA using differential pulse voltammetry. The voltammograms were registered from 0.0 to 0.5 V, at of 5 mV s^{-1}, in a Britton-Robinson buffer solution (pH = 7.0) using a potentiostat/galvanostat Autolab PGSTAT302N. The three-electrode system consisted of a carbon composite electrode (4 mm of diameter) as the working electrode, a Pt wire as the counter electrode, and SCE as the reference electrode. The samples were in the range of $1.5 \times 10^{-5} – 6.0 \times 10^{-3}$ mol L^{-1}, and identified as A1 to A7, from the most diluted to the most concentrated. The data was processed using the free software Chemostat for analysis by hierarchical clusters (HCA) and principal component analysis (PCA) [3]. The dendrogram obtained by the HCA in Figure 1, indicates four groups of concentrations: the first of the lowest concentration (A1), the second group corresponds to samples A3 and A4. The other groups are composed of the most concentrated samples, A5-A6, and finally A7. According to PCA, three main components explain the total variance, PC1 (97.1%), PC2 (2.8%), and PC3 (0.03%). The PC2 loading showed a small overlap attributed to a slight shift of the oxidation potential toward more positive values with increasing concentrations. PC3, on the other hand, shows a strong positive influence from the baseline that increases during the additions, which can be ascribed to the adsorption of the analytes between voltammetric analyzes, which can be corrected with an electrochemical cleaning step of the electrode.

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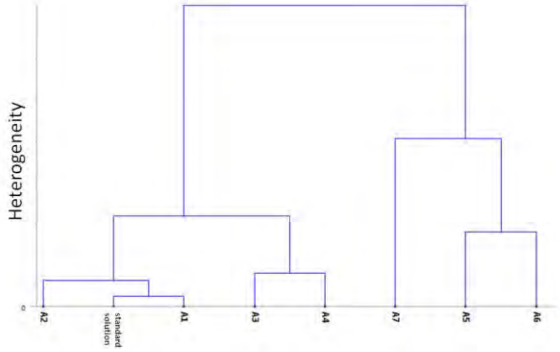

Figure 1. Dendrogram obtained by HCA. A1, A2, A3, A4, A5, A6 and A7 represent the seven successive additions of the analytes.

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V_2O_5 as a Promising Cathode Material for Aqueous Magnesium Ion Batteries

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In this work, the electrochemical performance of aerosol-assisted chemical vapour deposited vanadium pentoxide cathodes at 600 °C, is presented. The as-grown oxides indicate specific discharge capacity of 300 mAh g^{-1} with capacity retention of 92 % after 10000 scans, coulombic efficiency of 100 %, noble structural stability and high reversibility. The present study shows the possibility to grow large-area magnesium cathode material with extended cycle stability via the utilization of an aqueous electrolyte under a corrosive environment. This enhanced performance may be a combination of electrode morphology and adherence compared to previous work employing electrode's growth temperature at 500 °C.

Screen-printed modified electrode based on gold nano/microstructures and MoS_2 exfoliated for determination of lead (II)

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In the last decades, global pollution has experienced a significant increment as a direct consequence of anthropogenic activities. Among heavy metal, lead (II) ions are one of the primary pollutants that have a cumulative effect and several deleterious implications in human health [1]. As a result, alternative analytical methods apart from the classic ones needs to be developed, looking for reliability, rapidity, and low cost. In this sense, many electrochemical sensors are currently being developed, with great emphasis on the preparation of modified electrodes using various types of nanostructured systems [2,3]. The present work presents a modified electrode consisting of electrodeposited gold, exfoliated MoS_2, and gold nanoparticles deposited on the surface of printed carbon electrodes (SPE), Figure 1(A) shows the steps followed for the modification. Differential pulse anodic stripping voltammetry (DP-ASV) was employed to determine lead (II) ions, where the preconcentration step involved a potential applied of -0.8 V for 180 s under a stirring condition. After 5 s of equilibration time, a differential pulse voltammogram was recorded, using a pulse width of 50 mV, a potential ramp of 5 mV, and a scan rate of 40 mV s^{-1}. The electrolyte solution consisted of a 0.1 mol L^{-1} solution of H_2SO_4. Figure 1(B) depicts the modified and unmodified electrodes' responses in the presence of 5 µg mL^{-1} of lead (II) ions, for comparative purposes. The proposed modified electrode, named as SPE/Au/MoS_2/AuNPs, significantly increased the intensity of the anodic peak; this can be attributed to the enlargement of the surface area caused by gold nano/microstructures, that also may promote an improvement in electron transfer.

Acknowledgments. The authors thank the financial support of the INCT of Bioanalytical (CNPq/INCT), CNPQ, and CAPES.

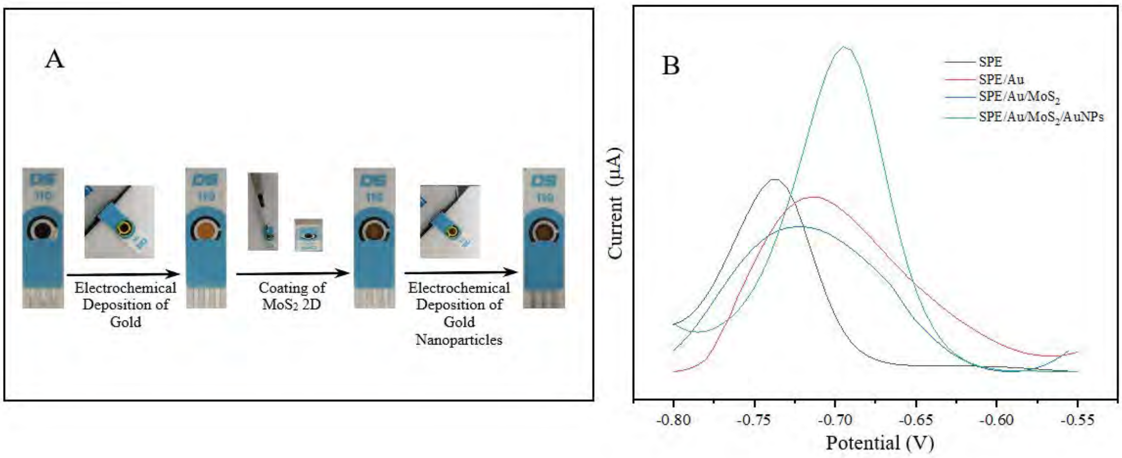

Figure 1. (A) Schematic representation of the modified electrode preparation. (B) Voltammograms obtained by DP-ASV at different modified electrodes in the presence of 5 µg mL^{-1} of lead (II) ions.

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Integration of Permeable Ceramic Baffles in Membrane-less Microbial Fuel Cells

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Microbial fuel cells can directly convert chemical energy in organic waste into electrical energy, which gives an excellent opportunity for renewable energy production, wastewater clean-up and elemental recovery. The rapid progress in the field has led to bringing this technology closer to application. One of the most promising approaches to boost MFCs implementation is the modular configuration of multiplied MFC units for usable electricity levels [1]. To achieve that, the anode and cathode location within the MFC bioreactor must be optimised to boost power performance by keeping the two electrodes in close proximity, i.e on the opposite sides of the Nafion membrane [2]. A cost-effective alternative to Nafion incudes porous ceramic materials as ion exchange membrane [3] where the permeability of the ceramic body allows for good ionic conductivity and sufficient cathode hydration.

This work presents the development of a novel, simplified design of a membrane-less MFC using a ceramic plate as a porous, permeable baffle between both electrodes that share the same electrolyte. A fully submerged anode and partially exposed to air cathode were attached to either side of the ceramic plate in order to keep the minimum distance, while maintaining electrical separation to maximise the output. Such a design was investigated in individual (large scale, 300 mm height) and stacked (medium scale, 100mm height) MFCs. Finally, miniaturised membrane-less reactors (30mm height) were compared with identical membrane-based MFCs where the ceramic functions as a membrane, fully separating the anolyte from the open to air cathode (Fig.1). This is to understand the role of the ceramic separator in a simplified and optimised construction for primarily power production in both membrane-based and membrane-less designs.

Results showed that a single large-scale MFC constructed from a terracotta floor tile produced up to 3.8 mW (1.9W/m^{3}) and successfully operated a small-scale dc motor while the cumulative power production from the medium-scale 6-unit stack reached up to 13 mW of power (6.5W/m^{3}) over 270 days of operation. A miniaturised membrane-less design showed similar or slightly increased raw (actual) power output up to 0.84mW (21W/m^{3}) in comparison to the membrane-based configuration that produced 0.75 (37.5 W/m^{3}) (Fig.1) which makes it a promising application for the membrane-less MFC stacks.

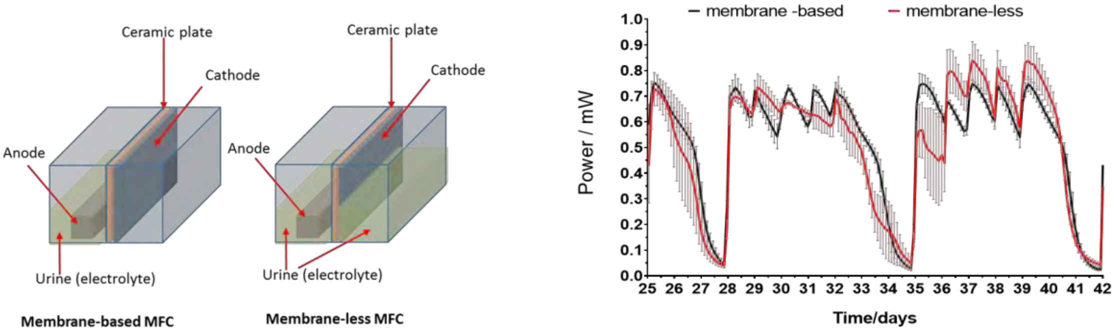

Figure 1. Miniaturised MFCs with ceramic plate functioning as a membrane in a membrane based design and as a permeable baffle in a membrane-less configuration. Power output comparison with error bars (n=3) between the two configurations.

Results showed increased performance with the scale-down of the reactor size and long-term stability, which is promising for future scale-up. The integration of ceramic baffles in membrane-less MFCs shows similar performance to membrane-based units. Scaling down MFC reactors in vertical height is of interest for the future development of multi-modular cascade systems maximising the number of modules that can be fitted within a single cascade therefore increasing the overall, usable power output of the stack.

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Impact of Mass Transport and other Parameters on the Measured Performance of Oxygen Evolving Catalysts

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The oxygen evolution reaction (OER) is a critical reaction for successful energy conversion. For instance, in water electrolyzers it predominately determines the energy demand for the production of green hydrogen. An optimization of this reaction is therefore very desirable. Electrocatalysts for the OER are typically measured as thin films (either made from powders or otherwise deposited), and for laboratory screening the rotating disc electrode (RDE) is the classical characterization technique.

The advantage of the RDE is supposed to be the controlled mass-transport towards the electrode. The OER is typically considered to be only little mass transport dependent, especially for the educts that are either water or OH^-, both available in excess. However, first reports indicate that there might be a limitation to this assumption, and also the transport of the produced O_2 can be a limiting factor.[1,2]

Here, we show the impact of mass transport in terms of rotation rate in the RDE and compare those results to complementary measurements in an electrochemical flow cell with various flow velocities. We will show that the use of a flow cell can improve the mass transport especially at higher current densities. Additionally, we address the importance of O_2-removal on thin layer electrodes with different hydrophobicity. These can for instance be achieved by the addition of different binders, i.e. ionomers that are used to stabilize the layer mechanically. However, besides affecting the hydrophobicity, we show that different binders can influence the electrochemical behavior by their own properties and current response. These results will illustrate how different experimental parameters can be interconnected and point out their influence on the measured activity of an electrocatalyst.

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RuO_2-WO_3/PAni: A Novel Nanocomposite for Energy Storage Applications

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Nanocomposites based on conducting polymers (CPs) and mixed transition-metal oxides (MTMO) have been shown distinguish properties, e. g. high specific capacitance and stability values. MTMOs, present multiple cations valence, which increase the electrochemical activity and the conductivity. Among metal oxides, ruthenium oxide (RuO_2) has higher capacitive response, but it is expensive and toxic, reducing severely its application.[1] In this way, we combined ruthenium oxide with tungsten oxide (WO_3), a transition metal oxide with unique electrochemical properties, in order to decrease the amount of ruthenium in the mixed oxide obtaining the RuO_2-WO_3. Combining this structure with one of the most studied conducting polymers (polyaniline - PAni), is an efficient tool to improve the polymeric conjugation and enhance the electrochemical performance of this system. In this way, we present the synthesis, characterization, and the electrochemical performance of RuO_2-WO_3/PAni nanocomposite. The synthesis the nanocomposite was performed by the in-situ chemical polymerization of aniline monomers in the presence of the presence of the previously synthesized MTMO. All the synthesized materials were characterized by spectroscopy and morphologic techniques, in order to ensure the success of the synthesis. Comparing the electrochemical performance of the RuO_2-WO_3/PAni to the neat PAni, we noticed a considerable variation in the capacitance values of 930 mF cm^{-2} for the nanocomposite and 100 mF cm^{-2} to the polymer. Once the good electrochemical performance for the RuO_2-WO_3/PAni was attested, we prepared some symmetrical energy storage devices, using the nanocomposites as electrodes. Theses devices showed good specific capacitance values and also the good stability. Finally, these results allow us to say that by the synergism of all the materials we were able to develop a novel nanocomposite with good capacitive performance. The authors acknowledges the Mackenzie Presbiterian Universisty (UPM), FAPESP (2018/02142-0, 2017/21988-5 and SPEC2012/50259-8), CNPq (403544/2016-5), Materials Chemistry Group (GQM – UFPR), LNNano and INCT of Carbon Nanomaterials.

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Circumneutral concentrated ammonium acetate water in salt electrolyte and argan shell derived carbon for green supercapacitor

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Supercapacitors (SC) are playing a central role in the transition to a green economy based on renewable energy sources and electric vehicles. The exponentially growing market of supercapacitor requires to replace flammable, volatile and toxic chemicals such as acetonitrile by cheap and environmentally friendly components.

Therefore, valuable strategies are the use of aqueous electrolytes and bioderived components such as biochar-based carbon that enable the valorization of wastes in a circular economy approach. Here we report about a physicochemical study and electrochemical characterization of a supercapacitor based on Argan fruit shell derived carbon electrode and a non-toxic super-concentrated aqueous electrolyte, i.e. a Water In Salt (WIS) solution of ammonium acetate.

Indeed, the utilization of WIS enables high voltage which are the main limitation of aqueous based electrolyte. The reported SC featured up to 47 F/g of specific capacitance and 4 Wh/Kg of specific energy at a temperature room temperature

To prove the practical applicability of this kind of electrolyte, electrochemical measure at into a wide range of temperatures (from -10 °C to 80°C), have been performed. This preliminary work aims at paving the way towards the design of novel green SCs based on non-dangerous aqueous based electrolyte and sustainable carbon sources.

Aknowledgements

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Air Stable Black Phosphorus-based Cathodes for Na-ion Batteries

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Notable progress in the field of electrochemical energy storage devices has been achieved due to the increasing exploitation of black phosphorus (BP) structure and properties. BP is highly unstable under O_2 exposure, which seriously limits its manipulation and consequent application. Thus, we have protected BP with polyaniline (PANI), leading to a stable and reliable material targeted for energy storage devices. For this purpose, BP-polymeric materials were synthesized through the liquid/liquid interfacial method, as previously described,[1,2] leading to thin, transparent and homogenous green films of BP/PANI nanocomposites. After Raman spectroscopy confirming the coexistence of both materials in the resulting film, both bare and capped materials were exposed to the same ambient conditions and evaluated through different techniques. Scanning electron microscopy (SEM) images and Raman spectra indicated the beginning of degradation of the uncapped material (without PANI) with only 3 days of exposure, while BP/PANI films have taken up to 60 days for the same process to begin, indicating a material 1500% more stable than the bare one. Electrochemical response and stability of BP/PANI nanocomposites were evaluated through cyclic voltammetry (CV) and charge-discharge (CD) studies (NaCl 0.5 mol L^{-1} pH 3), in order to evaluate energy storage properties.[3] Films of BP/PANI were evaluated and compared to pure PANI and BP, under air and inert atm ($N_{2(g)}$). CVs results have shown that all materials have the same behaviour after 200 cycles either with or without $N_{2(g)}$ purge. BP is degraded right after the first cycle, evidencing the expected low stability. BP/PANI, however, has evidenced the preservation of BP even after the 200 cycles under air, which was confirmed through post-characterizations. CD studies were performed from 0.5 A g^{-1} to 3 A g^{-1}, reaching capacities up to 200 mAh g^{-1} at 0.5 A g^{-1} rate with a coulombic efficiency of 100%, without compromising the integrity of BP in the films. To further explore the performance of the materials and understand the ion behaviour during the process, we analysed the electrodes through electrochemical impedance spectroscopy (EIS). In general, the obtained Nyquist plots evidenced a lowered resistance and improved diffusion properties of BP/PANI composite compared to neat polymer, corroborating with the best results verified in CD analysis. Aiming to investigate the competition between H^+ and Na^+ in BP intercalation during the electrochemical processes, we have also analysed the samples in pure 1 mol L^{-1} HCl (*i.e.* without Na). Unlike the previous case, similar profiles were found for BP/PANI and PANI, indicating equal performances towards H^+ insertion/expulsion regardless of BP presence. Thus, we can attest the interference and participation of Na^+ during BP/PANI processes in NaCl pH 3. **FIGURE 1** summarizes all described results. Overall, this work provides new possibilities heading for the development of oxygen friendly thin films to build new BP-based electrodes for sodium aqueous batteries.

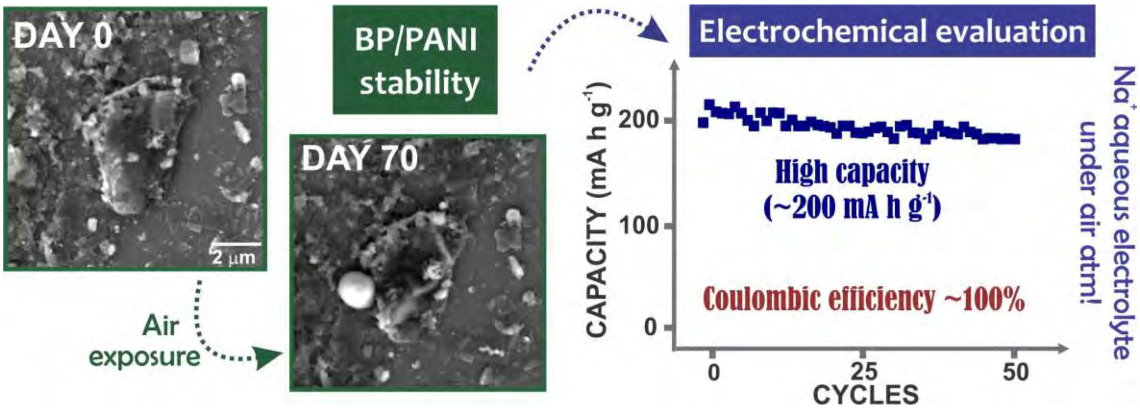

FIGURA 1. SEM images of BP/PANI composite and its capacity values over cycles.

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Alternative Me-N-C based Carbon Foams as Fe-free and non-PGM Electrocatalysts

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There is a demand for reducing the environmental load of automobiles to solve the current environmental problems. Fuel cell electric vehicles (FCEVs) which use hydrogen as fuel emit no carbon dioxide, and have already been commercialized. platinum-based materials are widely used as oxygen reduction reaction (ORR) catalysts. However, their high cost and limited durability impedes large-scale implementation. Until now, non-platinum group metal (non-PGM) Fe and N doped carbon (Fe-N-C) catalysts have achieved promising ORR activity [1]. However, these Fe-N-C catalysts still suffer from poor durability, due to the formation of reactive peroxide radicals as a side reaction during the ORR. Meanwhile, the use of Co species avoids the production of such radicals, potentially preserving the electrocatalyst [2]. Therefore, in this study we investigate the dependence of ORR activity on a variety of different metal ions by synthesizing alternative Me-N-C carbon foam electrocatalysts (Me = Co, Ni, Sn).

Pt-free electrocatalysts were synthesized from nitrogen-doped carbon foams (N-C) and various metal salt and small molecule precursors. Porous nitrogen-doped carbon foams with large surface area were made in-house. These were adsorbed with metal acetate and then heated in inert atmosphere, followed by acid washing to remove metallic phases. Finally, heat treatment under ammonia was performed. The effect of heat treatment temperature and metal loading on the microstructure and porosity was evaluated. The resulting catalysts were evaluated for catalytic activity using rotating-ring disk electrode voltammetry (RRDE) in acid.

For Co-N-C electrocatalysts it was found that heat treatment of the nitrogen-doped carbon foam support has a significant effect on catalyst performance, largely due to changes in surface area and porosity. The metal loading also has a strong effect on the performance, with an optimum Co loading of 0.1 wt% resulting in an onset potential of 0.8 VRHE and a half-wave potential of around 0.65 VRHE. Different metal ions were also systematically investigated, and it was found that Sn is highly promising as an alternative to Fe in non-PGM electrocatalysts. These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

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Influence of pH and current density on the generation of oxidizing species in the peroxicoagulation process with gas diffusion cathode

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Abstract

Peroxicoagulation process combines electrochemical generation of ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) for the production of hydroxyl radicals ($^\bullet OH$) in acidic medium by Fenton reaction (eq. 1-3), to oxidize organic pollutants in wastewater (Nidheesh, 2018; Brillas *et al.*, 1997). Nevertheless, not all the effluents present acidic conditions, requiring previous acidification before its treatment by peroxicoagulation process. This requirement could limit its application for the treatment of large amounts of water due to the increased demand for chemicals. Also, the current density could affect the pH of the medium, so it is important to know the influence of the pH and current density on the production of the different oxidizing species during the peroxicoagulation process.

$$Fe \rightarrow Fe^{+2} + 2e^- \tag{1}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{2}$$

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + {}^{\cdot}OH \tag{3}$$

In this research, H_2O_2 and $^\bullet OH$ production generated by peroxicoagulation were assessed. A two electrodes (3.1416 cm^2) electrochemical cell without division (50 mL of solution volume) was used, applying current densities of 3.2, 9.5, 15.9 and 22.3 mA cm^{-2} for 30 min of electrolysis, in a synthetic solution with initial pH of 3 to 9 and 0.05 M Na_2SO_4 as supporting electrolyte. For H_2O_2 generation assessment, a Ti/Pt anode and a graphite cloth-polytetrafluoroethylene (PTFE) gas diffusion electrode (GDE) as cathode were used. For $^\bullet OH$ generation assessment, an iron plate anode and a GDE as cathode were used. During all the experiments, the GDE was fed with pure oxygen at a flow rate of 1 L min^{-1}.

H_2O_2 was analyzed by UV/Vis spectroscopy using a HACH DR-6000 spectrophotometer via the Ti (IV) oxysulfate method (λ = 406 nm). For the $^\bullet OH$ detection, coumarin ($C_9H_6O_2$) was used as a probe compound, which reacts with $^\bullet OH$ resulting in the formation of the fluorescent adduct 7-hydroxycoumarin ($C_9H_6O_3$). The detection and quantification of 7-hydroxycoumarin were carried out using an AGILENT Cary Eclipse fluorescence spectrophotometer (λ_{ex} = 340 nm, λ_{em} = 456 nm and slit 5).

The results indicated that the increment of current density has a positive effect on the production of H_2O_2 at pH 3. However, increasing pH from 3 to 9 reduced almost 50% the H_2O_2 at 22.3 mA cm^{-2}.

Concerning $^\bullet OH$ radicals production, its concentration decreased with increasing pH, which is consistent with the decrement of H_2O_2 in the GDE cathode at higher pH. On the other hand, the increase in current density decreased the $^\bullet OH$ radicals generation. The highest production and stability of $^\bullet OH$ radicals during the 30 min of electrolysis was obtained with the lowest applied current density.

This study reflects the importance of the pH solution and the current density in the generation of H_2O_2 and $^\bullet OH$ radicals, making the application of peroxicoagulation process plausible for the treatment of wastewater.

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Modification of the Carbon Fiber Microelectrodes with Carbon Black for Dopamine and Serotonin Simultaneous Detection

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Adequate concentration of neurotransmitters in the neural structures is crucial for the proper functioning of the whole body. Due to the small size of brain structures and rapid nature of the neurotransmitters' transport[1] microelectrodes has been proposed as a suitable device for their measurement.

Carbon black (CB) is known for its excellent properties toward neurotransmitter detection[3]. Deposition of CB on carbon fiber has until now mainly been done by chemical vapor deposition[2]. In this study the possibility of CB deposition on microelectrodes from sol-gel solution was investigated.

Carbon fiber microdisk electrodes (CFMEs) with a 7 μm tip have been prepared. Electroassisted deposition under negative potential and dip-coating deposition from CB suspension in a polymeric matrix were tested. Scanning electron microscopy was applied for the analysis of the tip structure (Fig. 1). Cyclic voltammetry and differential pulse voltammetry measurements of dopamine (DA), serotonin (5-HT), uric acid (UA) and ascorbic acid (AA) were performed. Phosphate buffer solution (PBS) and Dulbecco's Modified Eagle Medium (DMEM) were used as a background solution to mimic the cell culture conditions. The distinction of overlapping DA and 5-HT signals[4] was the primary objective along with the interference and stability study in DMEM as secondary objectives.

During the electroassisted deposition, a thin layer on the surface of the electrode was produced, while after dip-coating a shell with multiple cracks was observed (Fig.1). Test measurements indicate stable microelectrode behavior of the CFMEs even a few weeks after preparation. Complete separation of DA and 5-HT signals on CFMEs with deposited CB was not achieved, although a new peak overlapping with the DA/5-HT peak was observed. CV studies showed that DA can be measured simultaneously with UA and AA without interference. The DA signal was linear in the concentration range 0.1 - 10 μM in PBS (R^2=0.99) and DMEM (R^2=0.96) on bare CFMEs, however on modified CFMEs signal was linear only in the range 0.1 - 1 μM in PBS and random in DMEM. 5-HT measurements showed low reproducibility on bare and modified CFMEs.

Detection of DA and 5-HT on CFMEs with deposited CB particles was achieved, however, the appearance of an additional peak might indicate incomplete covering of the electrodes' surface. Further investigation of proper CB deposition is essential. Other catalysts should be taken into consideration.

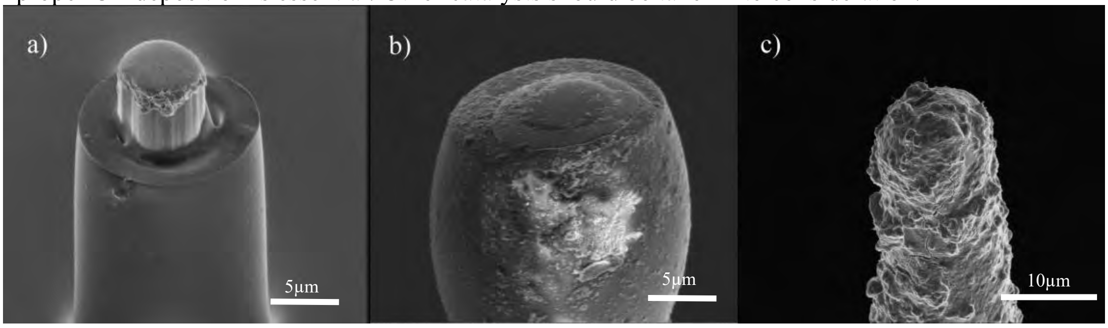

Figure 1. SEM images of the microdisk electrodes' tips: a) bare CFME during polishing b) CFME after electroassisted deposition of CB c) CFME after dip-coating deposition of CB

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EWN would like to thank Ann-Sofie Cans (Chemistry and Chemical Engineering, Chalmers University) for the training on fabrication of carbon fiber microelectrodes

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Characterizing and mitigating the degradation of oxidized cathodes during capacitive deionization cycling

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The surface chemistry of carbon electrodes plays an important role in capacitive deionization (CDI) cell performance. Applying appropriate surface chemical treatment to CDI electrodes results in an improvement of maximum salt adsorption capacity (mSAC) [1] and charge efficiency[2], yet the performance of the treated electrodes often decreases significantly during long-term cycling, and the surface group degradation mechanisms are not well understood. We here study the performance reduction of an oxidized cathode in order to investigate the degradation mechanism and enhance the stability of the treated cathode during long-term operation.

Single-pass CDI tests were conducted with flow-through electrodes, operated in constant voltage mode (1V). We investigate the degradation of a cathode treated with nitric acid (OC) and an as-received cathode (AC) for a feed water containing 20mM of NaCl salt for charged to equilibrium for 100 cycles. Further, direct acid-base titrations and surface chemistry analysis were performed before and after CDI cycle testing in order to diagnose degradation mechanisms. The cathode oxidation allows for an increase in the cell's initial mSAC from 8.2 mg/$g_{electrode}$ to 15.7 mg/$g_{electrode}$. However, mSAC decreases during cycling to 11.2 mg/$g_{electrode}$ by the 100th cycle (Figure 1a). As can be seen in Figure 2b, OC post-experiment titration curve is shifted to the right relative to the OC pre-experiment curve. This latter observation indicates functional group loss, due to a lower concentration of negatively charged functional groups in the micropore relative to the OC before CDI experiments.

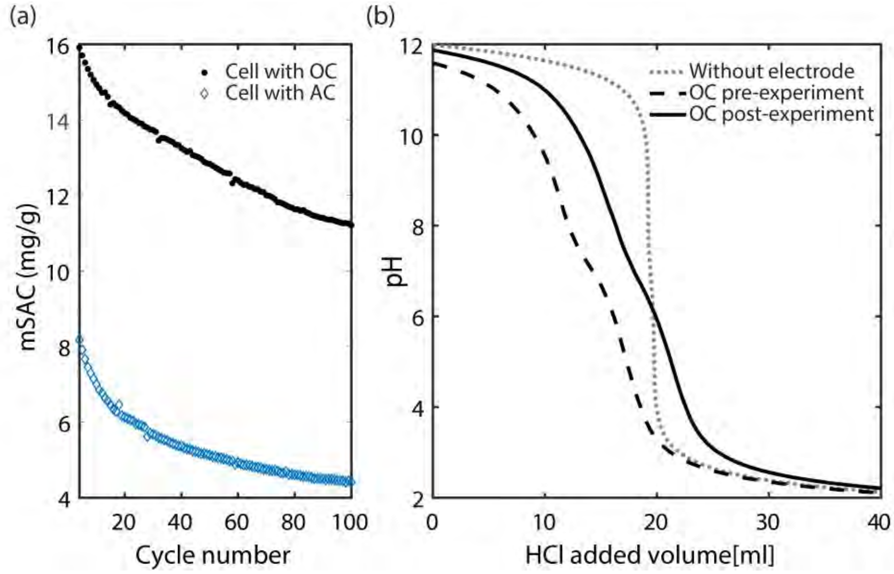

Figure 1- (a) Measured mSAC of cell with OC and cell with AC. The feed concentration is 20mM NaCl, the charging voltage 1 V, and discharge voltage 0 V. (b) Results of direct titration measurements for OC pre- and post-experiment. Also shown is the titration applied to a blank solution without electrode.

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Interfacial Degradation on Carbon and Non-Carbon Surfaces during the Oxygen Evolution Reaction

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The oxygen evolution reaction (OER) is the anodic half reaction occurring within a water electrolyzer. Its oxidative condition could negatively affect the surfaces of materials consisting of an anodic compartment. Choice of the materials is strongly dependent upon their electrical conductivity and (electro)chemical stability. Carbon and titanium are the most practical examples. However, they could also be deteriorated by the prolonged operation of the OER due to accumulated stress. Considering the overpotential required for the OER, carbon could be corroded to give carbon oxides and titanium could be passivated to form an insulating oxide layer. These interfacial degradation phenomena would lead to the physical loss or electrical disconnection of the catalyst from the surfaces, thereby decreasing electrocatalytic performances. For the long-term functioning of the OER, the interfacial degradation must be comprehended to avoid it. In this study, we deploy *operando* techniques of surface-enhanced infrared absorption spectroscopy (SEIRA) and controlled polarization tests in order to simultaneously observe the interfacial degradation during the OER. In advance of it, we elaborate upon the fabrication procedure of structures idealized for the *operando* observations. We synthesize iridium-embedded carbon nanofibers and iridium oxide-electrodeposited titanium foils. We disclose that during the functioning of the OER, carbon surfaces are irreversibly impacted whereas the interfacial degradation on titanium surfaces could be circumvented. Our results highlight that the future research on materials for OER compartments should aim at the surface engineering of non-carbon surfaces by which sufficient conductivity and stability can be imparted. The material selection process can be facilitated by the methodologies suggested in this study.

Lithium Polysulfide-Based Electrolytes for Li Metal Anodes

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Li metal batteries such as lithium–sulfur (Li–S) and lithium-air batteries have been strongly considered as the promising candidates for the next-generation energy storage devices. Unfortunately, as the result of the notorious Li dendrite growth inherent in these batteries upon repeated charge/discharge cycling, the concomitant serious safety concerns and low Coulombic efficiency have retarded their practical applications.

Herein, we report a facile but effective strategy to in-situ construct a stable and compact solid electrolyte interphase (SEI) layer to protect Li deposits by the synergetic effect of Li_2S_5-based ternary-salt (LiTFSI–$LiNO_3$–Li_2S_5) electrolyte. LiTFSI affords a high Li conductivity of the electrolyte in a working battery. The reactions between $LiNO_3$ and Li_2S_5 induce Li_2SO_3 formation, which is favorable to build protective SEI layer. Compared with routine LiTFSI mono-salt electrolyte, the Li_2S_5-based ternary-salt electrolyte renders Li metal anode (1) dendrite-free morphology, (2) improved Coulombic efficiency (94% compared with 60% in routine electrolyte), (3) suppressed polarization, and (4) prolonged lifespan (80 h compared with 20 h). These superior characteristics are attributed to the enhanced stability of the SEI layer by deliberately introducing the Li_2S_5 polysulfide as a pre-existing precursor, which, however, is always considered as an undesirable intermediate in Li–S batteries. Further development of this electrolyte enables practical applications for rechargeable lithium metal batteries, especially Li–S batteries.

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Open Circuit Potential and Ionic Transport of Neutralization Redox Flow Battery with Two Hydrogen Electrodes

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The development of low-cost and effective energy storage systems for renewable energy sources is an essential problem of the modern energy industry. At the moment, redox flow battery (RFB) is one of the most promising technology to energy storage in distributed energy grid. However, up to date, even the most studied vanadium RFBs have quite high cost due to the expensive vanadium electrolytes. In this work, a novel chemical power source - neutralization RFB with two hydrogen electrodes is developed. This RFB uses cheap and environmentally benign electrolytes - solutions of acid, alkali, and salt (fig. 1).

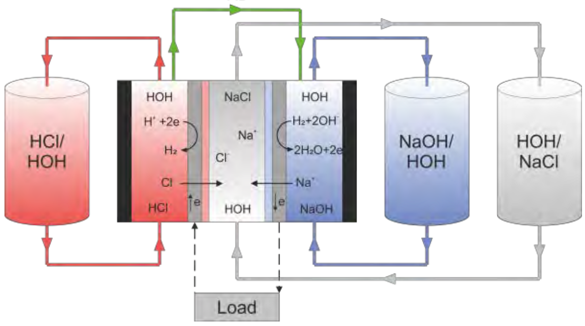

Figure 1 – Scheme of neutralization RFB with two hydrogen electrodes

In the course of the discharging process, acidic and alkaline solutions are neutralized due to hydrogen evolution/oxidation electrode reactions, while the salt solution at the middle compartment becomes more concentrated as a result of ionic fluxes of cations and anions. Thus, the overall reaction $H_3O^+ + OH^- = 2 H_2O$ gives 79.9 kJ per 1 mole of H_2O.

Several pH-dependent electrode reactions can be used as redox-component of neutralization RFB. We consider the hydrogen gas evolution/oxidation process for that purpose since the gaseous component (being the product of the cathode process and the reagent of the anodic one) can be easily transferred from cathodic to anodic compartments of the proposed cell. Anion and cation exchange membranes separating positive and negative electrodes from middle space are to prevent the leak hydroxonium and hydroxide ions and provide the ionic current of their counterions across the cell.

Energy can be obtained from neutralization of acid and alkaline solutions and saved employing the reverse process with a minimal loss if hydrogen evolution reaction and hydrogen oxidation reaction is carried out on reversible hydrogen electrodes in both acidic and alkaline medium.

The theoretical energy density of neutralization RFB using 4 M electrolyte solutions is 44 W·h/L [1]. Reported energy density and efficiency of existing neutralization batteries are modest compared to those of traditional RFBs [1, 2]. Advantages of proposed neutralization battery over analogs are the use of hydrogen as a self-supplied redox-component and two-membrane cell concept without bipolar membrane. The real energy output for discharge and round-trip energy efficiency of the cell has been determined for the laboratory-scale setup of 4 cm^2 membrane electrode assembly.

Acknowledgements: The work was supported by Mendeleev University of Chemical Technology of Russia. Project Number X-2020-010.

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Fe-N-C electrocatalysts for oxygen reduction reaction: facile synthesis strategy and stable performance in alkaline environment

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Platinum group metal-free electrocatalysts have shown promising features for catalyzing oxygen reduction reaction (ORR) at the cathode of different types of fuel cells [1-3]. However, high costs for synthesis, stability and activity issues under operating conditions, still limit their applicability. In our approach, Fe-N-C catalysts were synthesized from a nitrogen and iron wet impregnation of black pearls followed by pyrolysis steps. Three different nitrogen sources (dopamine, imidazole and benzimidazole), and two different pyrolysis atmospheres (Ar and NH_3) were used. The obtained materials were characterized in terms of structure, morphology, surface chemistry, thermal and electrochemical properties. Electrodes with a high porosity and accessible active sites were obtained tailoring the synthesis parameters, as indicated by Raman and X-ray photoelectron spectroscopies, cyclic (CV) and linear sweep voltammetry (LSV) with rotating ring disk electrode (RRDE). In particular, we found that the pyrolysis step under ammonia flow led to high double layer capacitance (CDL) electrodes (Figure 1a) and the use of imidazole as nitrogen-rich organic precursor improved ORR activity as compared to control Pt-based ones. In addition, the stability tests were carried out to evaluate the electrochemical active surface area (ECSA) changes after cycling 1000 times at a scan rate of 500 mVs^{-1}, with acquisition of CVs and LSV curves at 5 mVs^{-1} after every 200 cycles (Figure 1b) in alkaline pH, and the activity to ORR from RRDE experiments in the same measurements conditions with rotation speed of 1600 rpm (Figure 1c). The tests shown a stable activity after 1000 cycles of the electrocatalyst prepared using imidazole and pyrolyzed under ammonia atmosphere.

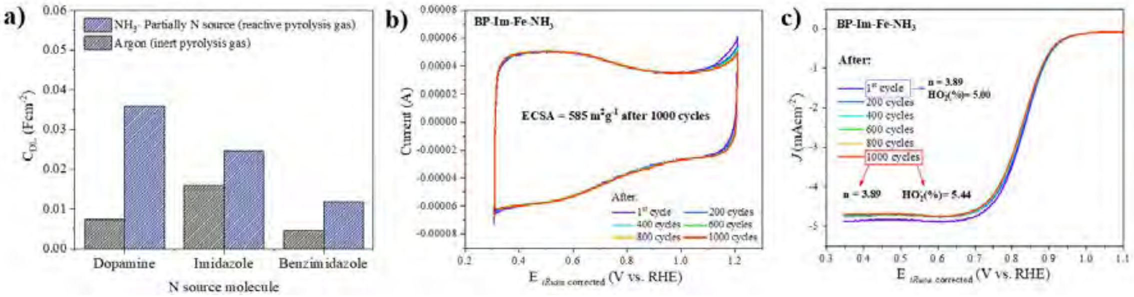

Figure 1. (a) C_{DL} of all synthesized catalysts, (b) cyclic voltammograms at a scan rate of 5 mVs^{-1} and (c) LSV curves at 5 mVs^{-1} and rotation speed of 1600 rpm in N_2 and O_2 saturated electrolyte (KOH 0.1 M) respectively, for the best performing material.

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Rational Design of Stable Solid Electrolyte Interphase for Li Metal Batteries

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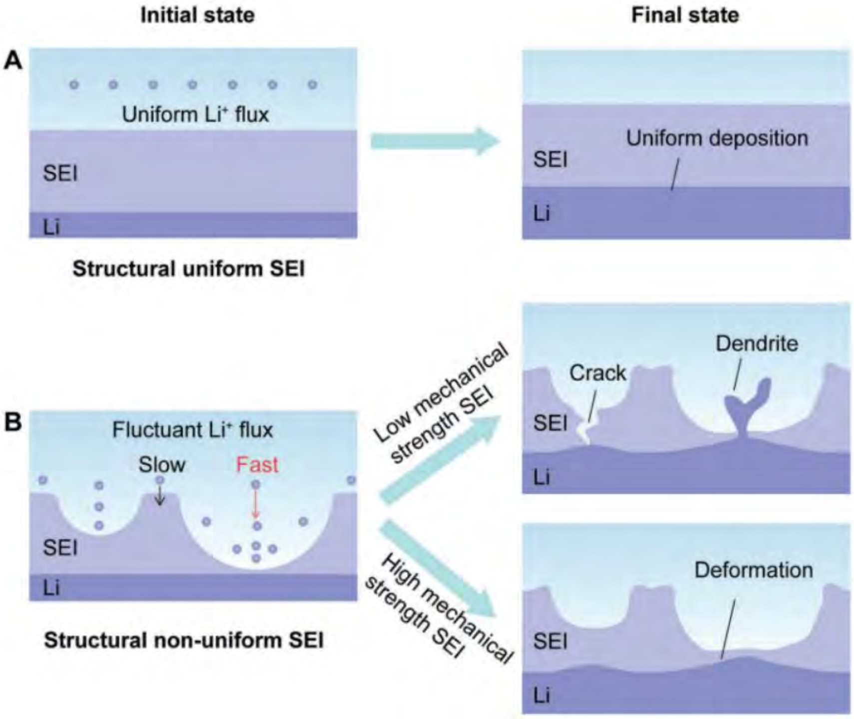
Rechargeable batteries, powering portable electronic devices and electric vehicles, play a pivotal role in sustainable development. Currently, lithium ion batteries (LIBs) are almost approaching to its ceiling of theoretical energy densities, and then the research of post-LIBs with high energy densities becomes urgent. Li metal has been spotlighted as a promising anode for next-generation rechargeable batteries due to its ultra-high theoretical capacity and an extremely low redox potential. However, its practical application has been hindered by Li dendrite growth, which renders a low Coulombic efficiency and short lifespan. A stable solid electrolyte interphase (SEI) is crucial in suppressing the formation of Li dendrites (Figure 1) [1]. In this work, a quantitative electrochemical–mechanical model that couples stress, diffusion, electric fields, and electrochemical reactions was constructed, successfully tracking the dynamical failure process of SEI. Furthermore, the impacts of structural uniformity and mechanical strength on the stability of the SEI under different working conditions were investigated. This work affords an insight into the rational design of stable SEI layers and sheds light on a possible pathway toward practical applications of Li metal anodes.



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Ultrasensitive Electrocatalytic Analysis of *Escherichia coli* at DNA modified Gold Electrodes

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Sensitive, specific and rapid detection of bacterial colonies is becoming the need of the hour. Food spoilage, prevention of pathogenic infections and antimicrobial resistance put such detection systems at highest priority in food and medicine industry. [1] Among these microbial communities, the bacterial strain of *Escherichia coli* (*E. coli*) is most commonly found, with pathogenic and non-pathogenic strains being biomarkers of bacterial contamination. [2] Here, we developed a novel electrochemical assay for *E.coli* utilizing DNA as electrical wires, mediating electron transfer between gold electrodes and a well-known DNA intercalator, Methylene Blue (MB).The binding of *E. coli* specific target DNA to the capture DNA-modified gold electrode surface triggers the intercalation of MB present in solution within the hybrid structure. The signal from MB is further electrocatalytically amplified in reaction with a commonly used redox indicator ferricyanide whose electrochemical reduction is otherwise very slow on the DNA-modified surfaces. The developed assay allows down to attomolar detection of both synthetic and isolated *E. coli* DNA and RNA. The high sensitivity of the assay allows direct application of it in point-of-care and industrial platforms for analysis of raw or minimally processed samples.

Keywords: Electrochemical detection, Methylene Blue, Escherichia coli

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An Amperometric Cholesterol Biosensor Based on the Synergistic Beneficial Roles of Prussian Blue and Gold Nanoparticles

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An amperometric cholesterol biosensor was designed using a glassy carbon (GC) electrode modified with a nanocomposite consisting of multi-walled carbon nanotubes (CNTs), ionic liquid (IL), Prussian blue (PB) and gold nanoparticles (GNPs).

Firstly, the GC electrode was modified with a bucky gel (BG) comprising CNTs and IL. Then, the PB and GNPs were co-electrodeposited on the surface of the BG/GC electrode. Afterwards, the Ni^{2+} ions were electrochemically incorporated into the PB structure in order to increase its stability in mild alkaline environment. Cholesterol oxidase was then immobilized on the modified electrode via a cross-linking method using glutaraldehyde.

Cholesterol was measured at −0.05 V vs. Ag/AgCl in 0.05 M phosphate buffer, pH 7.4. The cholesterol biosensor exhibited a high sensitivity of 173.56 $\mu A\ mM^{-1}\ cm^{-2}$ with a detection limit of 1.9×10^{-5} M and a linear range of $1.9\times10^{-7} - 2.8\times10^{-6}$ M. The proposed biosensor displayed a good storage stability of 1 month.

Keywords: Cholesterol, Biosensor, Carbon nanotube, Prussian blue, Ionic liquid, Gold nanoparticle

Study of the EC″ mechanism by cyclic voltammetry and chronoamperometry

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The development of new electrochemical power sources allows us to expand the capabilities of traditional energetics. One of the promising areas of modern electrochemical energetics is flow redox batteries, which generate electricity during the electrochemical reaction of energy-intensive liquid reagents. The use of bromates and chlorates as chemical oxidizing agents turned out to be promising, as this allows one to achieve high energy intensity and power density for a flow redox battery.

Nevertheless, until recently, the bromate anion was not considered as a promising reagent for electrochemical power sources due to its' non-electroactivity in the region of positive (vs SHE) potentials even on catalytically active electrodes. A few years ago in [1] the possibility of electroreduction of bromate anions in acidic media on carbon electrodes was shown due to the presence of trace bromine concentration.

In this case, the target gross process

$$LiBrO_3 + 3\,H_2 \rightarrow LiBr + 3\,H_2O$$

passes through a catalytic cycle consisting of a heterogeneous reaction on the electrode surface for a reversible bromine/bromide redox pair:

$$Br_2 + 2\,e^- \rightleftarrows 2\,Br^-$$

and irreversible (with high acidity of the solution) homogeneous reaction:

$$BrO_3- + 5\,Br- + 6\,H+ \rightarrow 3\,Br_2 + 3\,H_2O$$

This process demonstrates autocatalytic behavior and, by analogy with electrochemical redox-mediator catalysis (EC'), was called the mechanism of redox-mediator autocatalysis (EC″) [1].

The purpose of the work was experimental studies of the bromate reaction by basic electrochemical methods, an experimental verification of the mathematical model of the EC″ mechanism and the search of the main transport (diffusion coefficients) and kinetic (rate constants of a homogeneous chemical reaction) system characteristics.

During the study, series of experimental chronoamperograms and cyclic voltammograms of the electroreduction of sodium bromate in acidic media on electrodes of various nature were obtained. The voltammograms were used to evaluate the reversibility of the electrochemical stage of bromine electrooxidation. As a result of solving the inverse kinetic problem using the obtained experimental data, for the description of which an analytical model was applied, the values of the main process parameters were established.

Acknowledgments

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Electron Transfer Thermodynamics and Kinetics of Immobilized Human Cytochrome *c*: Effect of Tyrosine Phosphorylation

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Human cytochrome c (hC*c*) stands out as a target for post-translational modifications, such as phosphorylation, which are related to the onset of diseases like ischemia. Previous works with mimetic phosphorylated hC*c*, in which tyrosine 48 or tyrosine 97 were replaced by *p*-carboxy-methyl-L-phenylalanine (hC*c*-Y48*p*CMF and hC*c*-Y97*p*CMF, respectively), have demonstrated that phosphorylation provokes significant structural changes that can be related to mitochondrial dysfunction of this protein [1, 2].

In this work, we have carried out a detailed characterization of the thermodynamics and kinetics of the interfacial electron transfer of wild type hC*c* and its phosphomimetic variants adsorbed onto gold electrodes modified with self-assembled monolayers of ω-mercaptocarboxylic acids, by analyzing their voltammetric response as a function of scan rate and temperature at pH 7.

The redox behavior of immobilized hC*c* was found to vary strongly with temperature. In particular, the temperature dependence of the redox potential and the electron transfer rate constant for the wild type variant were observed to be biphasic, with a transition point at approximately 30°C. This behavior has been ascribed to a reversible conformational transition between two states of the oxidized form leading to a more opened heme structure with a weakened Fe-Met80 bond. Moreover, it is shown that immobilized hC*c*-Y48*p*CMF and hC*c*-Y97*p*CMF display more negative redox potentials than the wild type, with a steeper temperature dependence. Both the enthalpic and entropic terms are shown to contribute to the observed shift of their redox potentials towards more negative values than those of the native protein. At the same time, the electron transfer rate constant of the phosphomimetic mutants are also lower than that of the native protein at temperatures below 40ºC, with remarkably larger values of both the electronic coupling between the redox center of the mutants and the electrode and the reorganization energy.

Overall, the present results point to a key role of phosphorylation into the modulation of the mitochondrial function of cytochromes that has been rationalized in terms of changes in the internal electric field of the protein around the heme caused by the extra negative charge brought about by the phosphorylation process. Bearing in mind that the electrostatic binding between the protein and the negatively charged surface precludes the alkaline transition of the protein, as lysine residues are involved in these electrostatic interactions, and based on the obtained thermodynamic and kinetic parameters for protein reduction, the structural change experienced upon phosphorylation is rather consistent with an increased lability of the Fe-Met80 bond of the native ferric state, and a larger protein solvation and flexibility.

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Voltammetry of Polymeric Hybrid Materials of Platinum (IV) Organic Complex for Drug Application

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The electrochemical behavior of new organic lipophilic PtIV complexes, namely, cis-[bis-nitroxyethyl isonicotinamide-N]tetrachloride platinum(IV) (**1**) and e-amine-d-(4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl)-a,f-bis(octanoato)-b,c-dichloroplatinum(IV) (**2**) were investigated in DMSO and MeCN solutions on Pt, Au and glassy carbon electrodes by cyclic (CVA) and square-wave voltammetry (SWVA). The results were compared with those for a model system, namely, wide-spread drug cisplatin.

The water-soluble hybrid materials of compounds **1** and **2** were prepared via solubilization of these PtIV complexes by copolymer nanoparticles of N-vinylpyrrolidone with (di)methacrylates [1-3]. They were characterized by dynamic light scattering (DLS), TEM, UV-Vis, and IR-spectroscopy. According to TEM and DLS, the hybrid materials consist of spherical particles with a hydrodynamic radius mainly ~(50–60) nm. The water-soluble hybrid forms of these Pt(IV) complexes were studied in aqueous phosphate buffer solutions (PBS) by electrochemical methods. The results were compared with those for their free and hybrid forms in DMSO and MeCN, and found to be quite different. CVA and SWVA curves of the water-soluble polymer particles loaded by compounds **1** and **2** and free Pt(IV) complexes in DMSO contain 3 to 5 irreversible cathodic peaks until E ~ -(1.5-2.5) V, resp. In contrast, only two overlapped peaks were observed for 1 within the potential region in PBS during a sufficiently long time. The free radical moiety of **2** exhibited one-electron irreversible cathodic and one-electron reversible anodic peaks in MeCN, and their potentials were substantially similar to those for long-lived 4-acetylamino-2,2,6,6-tetramethylpiperidine 1-oxyl radical (**3**). This free radical moiety kept its redox characteristics at the same level as **3**. Electrochemical and non-electrochemical data testified in favor of the inclusion of Pt(IV) complexes in polymer particles that were quite stable in the aqueous medium during a sufficiently long time but subjected to destruction in non-aqueous solvents under study.

These prepared hybrid materials with antitumor activity [1, 2, 4] can be promising as potential drugs with controlled properties including, e.g., water-solubility, bioavailability, prolonged action, duration of circulation in blood, accumulation in tumors, toxicity and foci of inflammation.

Acknowledgments

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Electrochemical scanning tunneling microscopy studies on electrode/deep eutectic solvent interfaces

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A deep eutectic solvent (DES) is a mixture of a salt and an appropriate molecular hydrogen bond donor at certain quantity ratio. Like ionic liquids, DESs have the properties of low vapour pressure, non-flammable, wide electrochemical window, good conductivity and solubility. In addition, DESs are low cost and the preparation procedure is simple. As a novel class of eco-friendly solvent, DESs have already been proposed for applications in various fields, such as electrochemistry. [1-2]

High ionic strength and the existence of non-ionic hydrogen bond donor component make DESs involve multi-natured interactions including columbic interaction, Van de Waals molecular interaction and hydrogen bonding. The multi-natured interactions lead to the complexity of electrode/DESs interface. So far, fundamental investigations on the electrified interfaces in DESs remain limited.

In this work, potential-dependent electrode surface structures in different deep eutectic solvents were revealed by in situ scanning tunneling microscopic imaging, the preliminary results on surface reconstruction, etching and adsorption on single crystal electrode surface are reported.

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Conductivity and Stability of $BaCe_{0.7}Zr_{0.1}Y_{0.16}Zn_{0.04}O_{3-\delta}$ Electrolyte under Hydrogen and Wet Argon Atmospheres

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Cost effective hydrogen production is vital to many industries tied to the hydrogen economy. Perovskites, such as doped barium cerate and barium zirconate, have been investigated as proton conducting electrolytes for many industrial applications including fuel cells and steam electrolysers [1,2]. Barium cerate has a high protonic conductivity however, poor stability under CO_2 and H_2O containing atmospheres leads to rapid degradation. Oppositely, barium zirconate exhibits good stability under those environments however poor protonic conductivity makes it an impractical solution [3]. In this study, the conductivity and stability of $BaCe_{0.7}Zr_{0.1}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BCZYZ) has been investigated under both 5% H_2/Ar and 3% wet Ar atmospheres. The highest conductivity of $2.7\text{x}10^{-2}$ $S{\cdot}cm^{-1}$ is obtained at 711°C under 3% wet Ar. Area specific resistance (ASR) is similar in both atmospheres (4.0 $\Omega{\cdot}cm^2$ under 3% wet Ar and 4.1 $\Omega{\cdot}cm^2$ under 5% H_2/Ar) at 711°C. ASR increased at lower temperature, 511°C, and a new arc (with 4.45 $\Omega{\cdot}cm^2$ ASR and $2\text{x}10^{-8}$ F equivalent capacitance) is formed under 3% wet Ar, indicating a second phase formation. No second phase formation is observed under 5% H_2/Ar. ASRs of electrolyte are determined as 7.6 $\Omega{\cdot}cm^2$ and 8.2 $\Omega{\cdot}cm^2$ under 5% H_2/Ar and 3% wet Ar, respectively. The second phase formation/degradation of electrolyte is attributed to $Ba(OH)_2$ and/or $BaCO_3$ formations around 500°C under wet atmospheres. At elevated temperatures, ~700°C, $BaCe_{0.7}Zr_{0.1}Y_{0.16}Zn_{0.04}O_{3-\delta}$ exhibits both good protonic conductivity, and good stability for use in fuel cells and electrolysers.

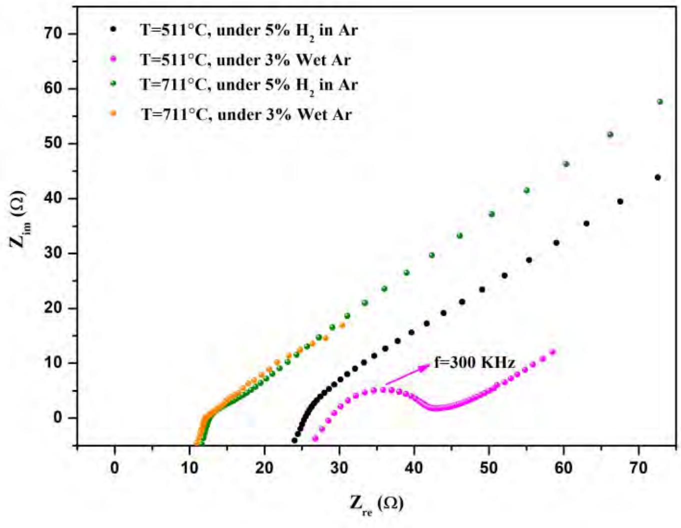

Figure 1. Impedance Spectra of BCZYZ electrolyte under 5% H_2/Ar and 3% wet Ar atmospheres

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Enhancement factors in EC-SOERS

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EC-SOERS (*Electrochemical-Surface oxidation enhances Raman scattering*) is a new phenomenon discovered in 2018, which enhances the Raman signal during the electrochemical oxidation of a silver electrode under particular electrolytic conditions[1]. This phenomenon has proven to be really useful in quantification of different organic compounds such as citric acid, uric acid or nicotinic acid[1–3]. Aiming to expand the knowledge on this phenomenon it is important to quantify the effectiveness of the SOERS substrate. Nowadays, achieving effective and reproducible SERS substrate remains a challenge; however, SOERS substrates emerge as a good alternative to classical SERS substrates in terms of stability and reproducibility.

Assessment of the enhancement factors (EF) is one of the best ways to study the performance of a SOERS/SERS substrate. EFs are usually calculated taking into account the number of molecules adsorbed on the surface of the substrate. Nevertheless, in EC-SOERS, which is a dynamic phenomenon, the silver surface is being oxidized during the experiment and, therefore, it is challenging to estimate the number of molecules adsorbed on the surface. Considering this limitation, the analytical enhancement factors (AEF) could be used instead of EF, in which the concentration of the sample could substitute the number of molecules adsorbed on the electrode surface[4] (eq. 1).

$$AEF = \frac{I_{SOERS} \cdot C_{Raman}}{I_{Raman} \cdot C_{SOERS}} \qquad \text{(Eq.1)}$$

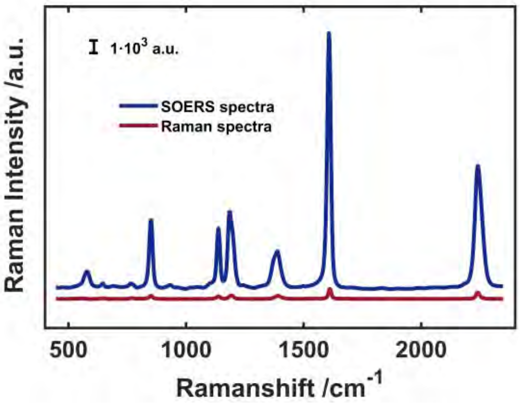

Figure 1. Ordinary Raman spectra of 0.9 M 4-CNBzA (garnet line), compared with EC-SOERS spectra of $2 \cdot 10^{-4}$ M 4-CN-BzA (blue line) registered at +0.40 V during a Raman-SEC experiment.

Since derivatives of benzoic acid are good candidates to evaluate the EC-SOERS effect, due to the presence of carboxylate group and delocalized charge around the benzenic ring, the assessment of AEF using such compounds have been carried out in this work. Figure 1 shows the comparison between the ordinary Raman spectra and the EC-SOERS spectra of 4-cyanobenzoic acid (4-CN-BzA). The intensity of these spectra is used in eq.1 to calculate the AEF of this molecule and a similar treatment is made with other isomers and derivatives of benzoic acid. A higher concentration of these molecules is necessary to have a measurable Raman spectrum whereas in EC-SOERS good spectra are obtained using lower concentrations.

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Simultaneous Electrochemical Removal of Nitrate and Terbuthylazine Pesticide from Low-Conductivity Groundwater

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The great intensification and centralization of agricultural and farming activities over the last decades to supply the increasing demand of food has entailed the accumulation of different types of organic and inorganic pollutants in soils and freshwater reservoirs as aquifers. Some of the former ones, mainly those with an anthropogenic origin such as pesticides or antibiotics are classified as contaminants of emerging concern (CEC) due to the uncertain associated ecological or human health impact. The pesticide terbuthylazine (TBA), a chloro-triazine, has become ubiquitous in the EU, being frequently detected in natural water bodies. TBA and its main by-product desethyl-terbuthylazine (DET) are toxic towards aquatic organisms and act as endocrine disruptors. Unfortunately, they are only partially removed by conventional water treatments [1]. On the other hand, the EU is the world's second biggest producer of pork after China and the biggest swine exporter. Pig farming involves the generation of large volumes of swine wastewater, with its associated intrinsic difficulties to get rid of it. Its disposal is getting currently under strict control in some of the most affected European countries such as Spain and Denmark, since it is a major source of nitrate in groundwater.

In recent years, several technologies have been developed for the removal of refractory organic pollutants. Electro-oxidation (EO) stands out among the eco-friendly electrochemical advanced oxidation processes (EAOPs) as the simplest method, with high ability to produce hydroxyl radicals ($^{\bullet}OH$) adsorbed on the anode surface. Coupling a highly efficient anode for EO with a suitable cathode that allows the simultaneous nitrate electroreduction in groundwater has been the aim of this work. This is not a straightforward task, since such water has low conductivity and contains Mg(II) and Ca(II) ions that can precipitate mainly as $CaCO_3$ and $Mg(OH)_2$ on the cathode surface, eventually causing its fouling. In practice, this is detrimental regarding the electrocatalytic properties of the cathodic surface and results in an excessive cell voltage increasing the energetic cost and making the treatment not economically viable.

This communication reports the performance of an electrochemical system developed on the basis of our previous studies [2,3]. The cell consisted of two mesh electrodes, i.e, Nb/BDD (mainly) or DSA$^{®}$-Cl_2 (for comparison purposes) anode coupled with a custom Fe mesh cathode, separated 3 mm to treat 500 mL of solutions containing 5 mg L^{-1} TBA and about 100 mg L^{-1} nitrate. The experiments were carried in two different water matrices: (i) simulated groundwater, mimicking the main characteristics of an actual groundwater in presence and absence of chloride anion, and (ii) the actual groundwater, which has been conveniently softened prior to the electrolyses. Large percentages of both, cathodic denitrification and EO of the pesticide, were attained at different current densities from 5 to 30 mA cm^{-2}, decreasing their concentrations below human consumption thresholds. The concentration of the main products and by-products were followed over time.

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Understanding the Effects of Self-Assembled Monolayers and Metallic Structure on Direct Electron Transfer of Fructose Dehydrogenase on Au(111) and Nanoporous Gold Electrodes

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Direct electron transfer (DET) between an electrode and redox/catalytic center(s) in oxidoreductases is a core "elementary" process in enzyme bioelectrochemistry.[1,2] Favourable orientation and high enzyme loading on electrodes are paramount in DET-type bioelectrocatalysis to ascertain high catalytic activity and ET rate.[3] Fructose dehydrogenase (FDH) from *Gluconbacter japonicas* is a membrane-bound oxidoreductase with three subunits, subunits I (67 kDa), II (51 kDa) and III (20 kDa).[4] Subunit I holds a flavin adenine dinucleotide (FAD) cofactor as the active center of two-electron fructose oxidation to 5-keto-D-fructose. Subunit II carries three heme *c* moieties, serving as ET relays between electron acceptors and FAD. Subunit III has no redox center and possibly contributes to structural integrity of enzyme.

We present here systematic investigation of the effects of both self-assembled molecular monolayers (SAMs) and nanoporous (Au-)electrode structure on DET-type bioelectrocatalysis of FDH absorbed on SAM-modified Au(111) electrodes. Two different SAMs with varying functional terminal-groups and alkyl chain lengths were studied. FDH on a 2-mercaptoethanol (BME) SAM showed the best DET performance with a maximum current density ($\Delta j_{\mathrm{max,det}}$: 54.88 ± 3.03 μA cm^{-2}) and DET-capable fraction derived from $\Delta j_{\mathrm{max,det}}$ over mediated $\Delta j_{\mathrm{max,met}}$ (χ_{det}: 13.33 %) due to the most favourable FDH orientation on the electrode surface. FDH on Au(111) functionalized with 3-mercaptopropanoic acid (MPA) SAM exhibited the best mediated ET with Δj_{max} of 640.76 ± 7.65 μA cm^{-2} using ferrocenemethanol as the mediator. This can be explained by the negatively charged SAM surface efficiently adsorbing FDH. Non-linear fitting to the electrocatalytic profiles was performed. The FDH catalytic properties strongly depend on the alkyl chain length, showing significant decrease with increasing SAM carbon chain length. Nanoporous gold supported FDH was also prepared. Porous gold structures not only improved the catalytic performance by increased enzyme loading and χ_{det}, but also increased notably the operational stability.

Acknowledgments

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Noise Measurements During Charging of Lithium Metal Anode Reveal Uneven Growth

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Electrochemical noise measurements are well known in the corrosion literature where the noise that is to be measured is appreciable in amplitude.[1] From the measured noise of corroding systems it is possible to identify the mode of corrosion and distinguish between localized corrosion from the uniform. Our group has previously shown that non-rechargeable batteries with Li / MnO2 chemistry shows increase in voltage noises after being exposed to a short circuit.[2] In our further studies, batteries were opened in nitrogen environment to determine the source of the increase in the noise level of the battery and the chemistry of the battery was examined using the necessary characterization methods. As a result of this research, which was inspired by the corrosion literature, it was observed that the pure lithium metal on the anode surface of the batteries exposed to the short circuit reacted inhomogeneously. No noise increase was observed in the noise measurements made in the slowly-discharged batteries, but it was also observed that the pure lithium metal on the anode surface of the battery decreased homogeneously. In light of the findings obtained, it shows that the increased noise level with the short circuit is caused by the anode / lithium metal of the battery cell rather than the changes on other battery components such as the corrosion of existing collectors.[3] It is known that charging of a battery with a metallic lithium anode causes the lithium metal to settle unevenly on the anode surface, resulting in the formation of lithium dendrites and/or mossy structures. Growing lithium dendrites can disrupt the separator separating the anode from the cathode, exposing the battery to a short circuit or even causing the battery to burn or explode. For this reason, the pre-detection of any dendrite formation that may occur in the anode of the battery is both academically and industrially important. Some preliminary studies show that noise level increase drastically after it is charging and discharged. (Figure 1) Just like noise measurements on non-rechargeable batteries with lithium chemistry exposed to short circuits, it is worth studying noise measurements during charging and discharging cycles in lithium batteries that are prone to form dendrite. Some other preliminary noise measurements on Lithium anode indicated that noise levels increase after charge and discharge cycles. In this presentation, we will first explain the details regarding electrochemical noise measurements and continue to investigate the origin of increase in noise levels in Lithium anode. We will present optical and electron microscopy to correlate the noisy features in noise measurements with mossy and dendritic structures that forms during the charge and discharge processes.[4]

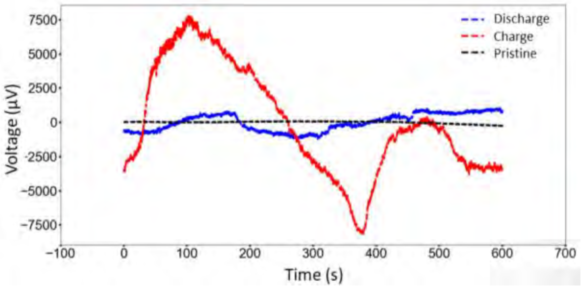

Figure 1 The noise measurement of pristine CR2032 (black) and the noise measurement of CR2032 after charged (red), and discharged (blue)

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Methodological Considerations in Simulating Dynamic Electrochemical Interfaces and Reactions from Density Functional Theory

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Atomistic density functional theory (DFT) based simulations of electrochemical interfaces and reactions have become irreplaceable as a complementary method in the rational development of sustainable approaches to energy conversion and storage. The field of computational electrochemistry is, however, still in its infancy and applied models require careful benchmarking for precise physicochemical predictions. Particularly, the importance of explicit solvent dynamics remains to be rigorously assessed. Considering the highly dynamic nature of electrochemical interfaces, a proper sampling of finite-temperature fluctuations by means of density functional molecular dynamics (DFTMD) may indeed be highly important.

We have explored the influence of interfacial dynamics on the potential energy surface of the Volmer–Heyrovský hydrogen evolution mechanism on a nitrogen doped carbon nanotube[1], as well as in simulating the potential-dependent hydrogen adsorption isotherm of single-crystal Pt(111)[2]. In both cases a thorough comparison with corresponding static approaches, namely the nudged elastic band (NEB) method and the computational hydrogen electrode (CHE) formalism, is performed. In the former we demonstrate decisive competing effects of solvent reorganization and entropy on activation and reaction free energies which are observed to *decrease* considerably compared to minimum energy paths obtained by static NEB calculations. Although the entropic contribution is intuitively expected to *increase* the energies, the relaxation of steric hindrance is found to dominate in the DFTMD simulations as compared to the problematic frozen solvent model conventionally employed in NEB transition path optimizations.

However, DFTMD simulations of dynamic water–adlayer structures on hydrogenated Pt(111) suggest that the determination of potential-dependent hydrogen adsorption isotherms is complicated by the challenging description of hydrogen and water co-adsorption on Pt(111) at intermediate hydrogen coverages. This balance appears particularly delicate, critically influencing electrostatic properties. Underestimation of water chemisorption by the employed RPBE-D3 functional is indeed found to overestimate sampled electrode potentials due to impeded charge transfer to the metal surface, thus demonstrating the necessity of an accurately converged interfacial structure. Conversely, the CHE scheme is found to reproduce the experimental isotherm with a surprising accuracy, thereby displaying the persisting value of carefully employed static, solventless approximations when considering the energetics of hydrogen chemisorption on single-crystal platinum. The influence of solvation and dynamics is nevertheless expected to remain significant in non-equilibrium reaction path simulations, as demonstrated in the previous direct simulation of the Volmer–Heyrovský mechanism.

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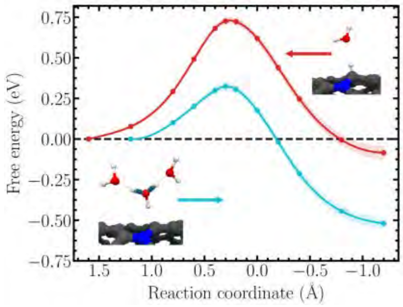
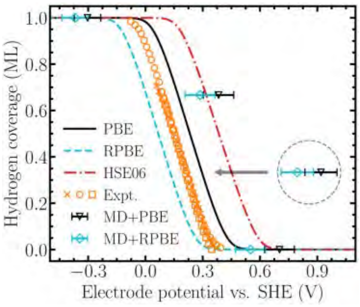


(a) Free energy profile of hydrogen adsorption at a dynamic NCNT–water interface using two different constraint definitions



(b) Hydrogen adsorption isotherms of Pt(111) as derived based on static and dynamic models at different levels of density functional theory

Feluric Acid Electropolymerization for a Novel Glucose Biosensor

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In this work, a polymeric membrane based on 3-methoxy-4-hydroxycinnamic acid (feluric acid) has been used for glucose oxidase immobilization onto carbon paste electrode by electrochemical polymerization. Feluric acid, is the most abundant hydroxycinnamic acid in the plant world, due to its autoinflammatory, anticancerogenic and antioxidant properties, it has been widely used in the pharmaceutical and food industries [1-3], due to its properties and redox behavior, we used feluric acid for the development of a polymeric film for a glucose biosensor.

The membrane has been synthesized by cyclic voltammetry at scan rate of 20 mV/s in acetates media 100 mM, pH 7.05 ± 0.5, in 2 mM of feluric acid, by utilizing this approach the enzyme has been entrapped into the polymeric membrane in a single step generating a glucose biosensor. The figure 1A, shows the typical cyclic voltammogram for the polymerization, it can be observed that after the first cycle the currents decreases as the usual behavior for the electropolymerization compounds with phenolic rings [4]. The biosensor has been evaluated for glucose response at constant potential of 800mV in phosphate buffer 100 mM, pH 7.34 at room temperature, the glucose biosensor shows a sensitivity of 36.1 nA/mM, linear response in the range from 0 to 30 mM covering the glucose dynamic range of clinical relevance. The 90% of the glucose response is achieved after 60 s for all the glucose dynamic range, the detection limit is 0.01mM. The figure 1B, shows the calibration curve for glucose biosensor with successive additions of glucose in 5mM increments. Figure 1C, shows the response stability for the calibration curve; all the measurements were measured vs $Hg/Hg_2SO_{4(sat)}$ electrode.

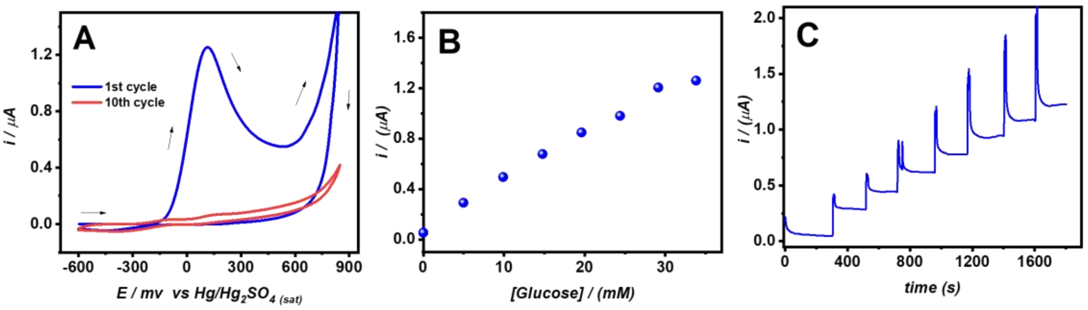

Figure 1. A) Cyclic voltammetry for feluric acid – glucose oxidase electropolymerization, 1st and 10th successive cycles at scan rate of 20mV/s. B) Calibration curve for glucose biosensor. C) Chronoamperometry for successive additions of glucose in 5 mM increments.

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Study of two-phase electrogenerated microfluidic flows

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The aim of the project is to certify the phenomena involved at the microfluidic scale in the production of electrogenerated bubbles, and to improve the efficiency of the electrolytic process by acting on the wettability and geometry of the electrodes. This study aims to validate the experimental results provided in the literature by using a multiphase model based on the VOF-HF (volume of fluid - heigh functions) method, which allows to model interfaces with variable surface tension and to limit the usual errors of multiphase models at micro-fluidic scales (parasitic currents, volume conservation).

Usually a force balance is done to predict bubble detachment. However, to be accurate this balance must include the Marangoni forces (FM) generated by the variation of the surface tension of the gas-electrolyte interface and due to the concentration and temperature gradients around the bubble [1].

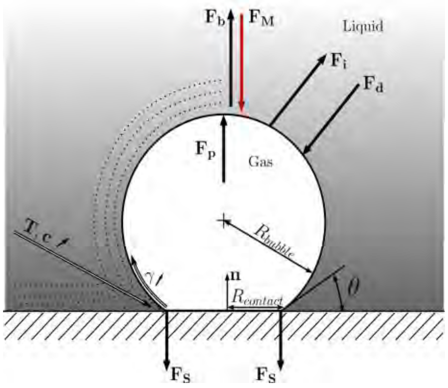

Figure 1 – Force balance made on a electrogenerated bubble on a micro-electrode

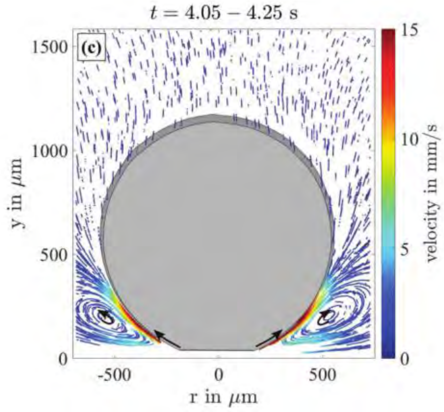

Figure 2 – Extract from [1], Marangoni effect around an electrogenerated bubble, captured using the Particle Tracking Velocimetry technique.

The Marangoni effect results in a micro-convection motion generated at the interface by the tangential stress due to the variation of the surface tension. To avoid numerical errors (parasitic currents, volume conservation problems) which are not negligible at the microfluidic scale, a robust numerical model must be used. An interface model based on "Heigh function" implemented in a "volume of fluid" (VOF) method was chosen, which allows to limit parasitic currents and to model the Marangoni effect. Numerical modelling is carried out using the ANSYS Fluent software (Pennsylvania, USA) which provides a basis for multiphysical modelling. The implementation of the interface model is based on user functions programmed in C language.

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Dendritic Sensor for the Simultaneous Detection of Ethambutol and Isoniazid in TB Treatment

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Tuberculosis (TB) is an airborne disease that is one of the most infectious diseases in the world. It is specifically a problem in South Africa due to the high number of HIV cases present. The World Health Organisation has stated in a recent report that South Africa is on its way to meet the milestone of managing TB to some extent and that is an even greater reason to focus on the patients still battling with this disease [1]. TB affects the lungs, but can also affect other part of the body such as the abdomen, central nervous system and bones and joints. These different parts of the body require their own type of treatment regime of TB drugs and periods of treatment [2]. There are four first line drugs that are used in the treatment of TB that are isoniazid, pyrazinamide, rifampicin and ethambutol. If a patient is unable to take one (or a few) first line drug(s) due to the drug resistance of their TB, then a regime is made up with the other first line drugs with the incorporation of second line drugs [3]. Dosages for TB drugs are prescribed by the patient's weight and not by the type of metabolism the patient has; i.e. the more a patient weighs, the higher the dosages they are told to consume. If the patient metabolises the treatment regime too fast then it is clear that a more frequent dose of the drugs are required whereby for a slower metaboliser, a less frequent dose is needed to give the patient's body time to use up the drugs. The quantification of TB drugs is needed to check how much is present in after the patient has taken them. Determining the concentration of these drugs in the patient's body allows for information on the type of metabolic profile the patient has. Standard methods used for detection of compounds as well as for their quantification requires some sort of sample preparation or is quite bulky and not fit for crowded hospitals. These methods include chemiluminescence, mass spectrometry and electrophoresis [4]. This is why electrochemical detection methods are looking more promising, especially in the case of crowded hospitals because of its small size and point-of-care features. The monitoring of how fast or slow a patient is able to metabolise the respective TB drugs is relevant since the effectiveness of the drugs in the treatment regime can be observed this way. A step forward is presented in this study whereby a dendritic sensor is used to simultaneously monitor two of the first line drugs (isoniazid and ethambutol) in phosphate buffer since with TB treatment there are many drugs to be taken by the patient. The setup involved a three electrode electrochemical cell whereby the Au working electrode was drop coated with the dendrimer and used to monitor additions of various standards containing different concentrations of isoniazid and ethambutol. This approach is one of the ways to make TB treatment more effective for TB patients.

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Simulation and Optimization Method for Alkaline Water Electrolysis

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In the context of global warming and intermittent renewables energy integration, hydrogen production via alkaline water electrolysis is a promising CO_2-free energy storage. However, this process produces expensive hydrogen and suffer from high inertia. Therefore, this study is focused on the optimization of the process using CFD simulation to solve those problems. The price of the hydrogen is due to initial investment (IC), energy cost (EC) and the cell voltage U_{cell} Eq(1-3).

$$\mathrm{CAPEX} = 2\ F\ IC\ T^{-1}\ S^{-1}\ M_{H2}^{-1}\ j^{-1} \tag{1}$$

$$\mathrm{OPEX} = EC\ U_{cell}(j)\ F/3600 \tag{2}$$

$$U_{cell}(j) = E_{rev} + R\ j + \eta_{act}(j) + \eta_{conc}(j) \tag{3}$$

With T the life-time of the electrolyzer in s, F the Faraday's constant in C mol^{-1}, j the current density in A m^{-2}, M_{H2} the molar mass in kg mol^{-1}, E_{rev} in reversible tension in V, R the ohmic resistance in Ohm m^2, h_{act} and h_{conc} respectively the activation and concentration overpotential in V.

In industrial electrolyzer, an acceptable cell tension is 2V to 2.2V with a reversible tension between from 1.15 to 1.23V. The activation overpotential is the energy needed to overcome the activation energy of the reaction, it can be decreased using a performant electrocatalyst. Because the concentration overvoltage is negligible. The other way of improvement is to decrease ohmic resistance by finding the perfect design.Owing to find the minimum cell voltage, a two-fluid model has been developed and compared to experimental data from Boissonneau et al [1] and other models. This model takes into account the momentum conservation for all the phases, charge conservation. The flow is taken as isothermal and the species gradients are neglected. The standard model developed by Fluent does not reproduce the experimental flow. The current model reproducing the experimental data, it could consequently be used. The optimization has been performed using the Vaschy-Buckingham theorem and design of experiments. Special efforts have been made to find the optimum inter-electrode distance (Figure 1). Finally, a simple technical and economical approach has been used to find the optimum working conditions using a genetic algorithm.

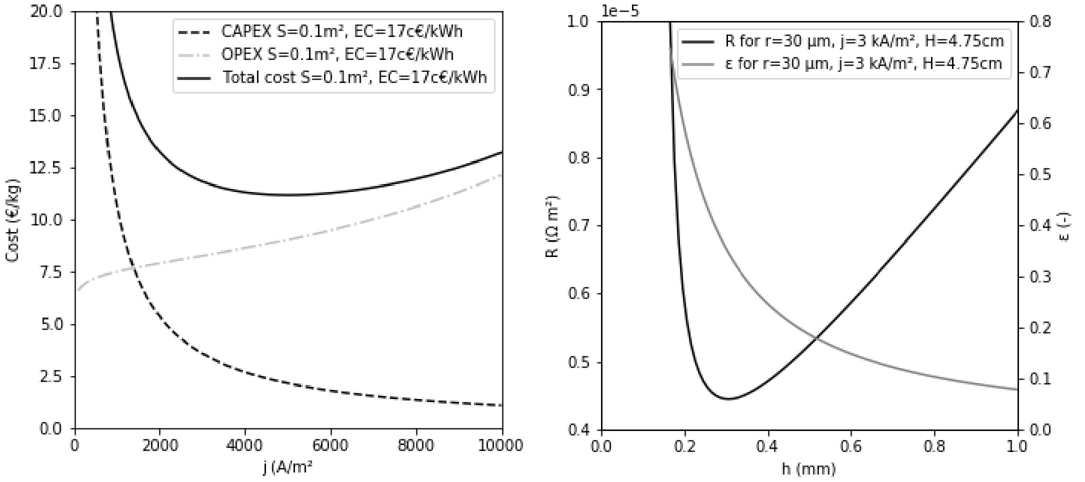

Figure 1-CAPEX, OPEX and total cost of hydrogen in € kg^{-1} (left) and ohmic electrolyte resistance and void fraction depending on the interelectrode spacing.

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CYP phenotype biosensor for detection of TB drugs in spiked real samples

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Tuberculosis is a respiratory disease that has plagued the globe for decades. Treatment for the disease has been available, however the disease remains one of the leading causes of death in the world, more prominently so in under-developed countries. One of the reasons for this is that patients suffer from adverse drug reactions (ADR's), which cause them to not complete the 6-month course of treatment [1]. Another reason is the unavailability of efficient treatment in rural areas. A mobile technology, which reduces ADR's is thus needed.

Portable electrochemical sensors for the detection of TB and the drugs used to treat it have been successful in the past [2] [3]. The development of biosensors are hindered by their efficiency in real life applications or complex matrices. Therefore, this study involves the development of a biosensor for detection of TB drugs in both synthetic urine and plasma. A simple sensor was developed using a metallodendritic electrocatalyst and a CYP3A4 enzyme immobilized onto the surface of a gold electrode. Smart nanomaterials such as this copper based first generation dendrimer allow for a higher surface area and conductivity of electrode surface for a highly sensitive sensor. The CYP3A4 enzyme was selected since it is a largely diverse enzyme in that it metabolizes up to 50% of all prescribed drugs and would mimic the bodily reaction sufficiently. The presence of a biological recognition element in an electrochemical sensor also allows for a much lower limit of detection (LOD) to be achieved.

The sensor was successful in detecting first line TB drugs in standard buffer as well as complex bodily fluids or matrices. In this case, the LOD ranged from 0.165 µM to 0.884 µM in both synthetic urine and plasma. Recovery studies when using real tablets in these complex matrices also yielded excellent results with an average recovery of 96%. The development of phenotype biosensors such as this is vital in tackling a disease that is so rampant in South Africa specifically. The possibility of determining metabolic profile of individual patients will aid in the fight against TB which is a part of the national development plan of South Africa [4]. Electrochemical sensor technology allows for a rapid testing which occurs at the point of care with minimal sample preparation. All of which are huge benefits when treating TB in rural areas i.e. townships or remote villages of Africa. Once a patients metabolic profile is determined, the dosage of treatment can be adjusted for fast, slow or intermediate metabolizers. Resulting in a more efficient treatment that avoids toxicity and adverse drug reactions and improves the quality of life for TB patients.

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Mediator-free SECM for probing the diffusion layer pH with functionalized gold ultramicroelectrodes

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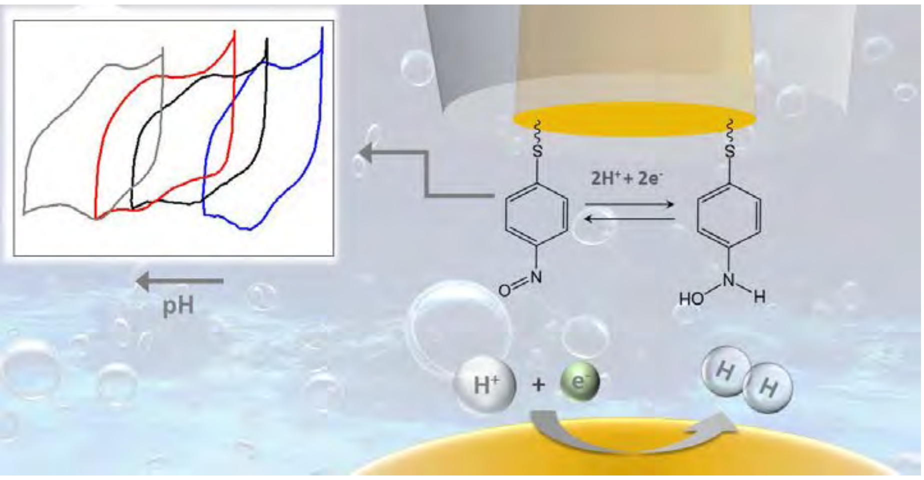
Probing pH gradients during electrochemical reactions is important to better understand reaction mechanisms and to separate the influence of pH and pH gradients from intrinsic electrolyte effects. Here, we develop a pH sensor to measure pH changes in the diffusion layer during electrochemical reactions. The probe was synthesized by functionalizing a gold ultramicroelectrode with a self-assembled monolayer of 4-nitrothiophenol (4-NTP) and further converting it to form a hydroxylaminothiophenol (4-HATP)/4-nitrosothiophenol (4-NSTP) redox couple. The pH sensing is realized by recording the tip cyclic voltammetry and monitoring the Nernstian shift of the mid-peak potential. We employ a capacitive approach technique in our home-built Scanning Electrochemical Microscope (SECM) setup in which an AC potential is applied to the sample and the capacitive current generated at the tip is recorded as a function of distance. This method allows for an approach of the tip to the electrode that is electrolyte-free and consequently also mediator-free. Hydrogen evolution on gold in a neutral electrolyte was first studied as a model system. The pH was measured with the probe at constant distance from the electrode (ca. 75 µm) while the electrode potential was varied in time. In the non-buffered electrolyte used (0.1 M Li_2SO_4), even at relatively low current densities, a pH difference of three units is measured between the location of the probe and the bulk electrolyte. The time scale of the diffusion layer transient is captured, due to the high time resolution that can be achieved with this probe. The sensor has high sensitivity, measuring differences of more than 8 pH units with a resolution better than 0.1 pH unit. The probe was also used to perform direct pH measurements in the diffusion layer during CO_2 reduction. pH measurements show how bicarbonate can buffer the interface and maintain the pH approximately 7 within a certain potential/current range, before extreme alkalinity starts to develop.



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Bragg coherent diffraction imaging for in situ/operando electrochemical studies: advances and future challenges

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Several new research topics and technological developments in electrochemistry were born in the last decades together with the progress of nanoscience and nanotechnology. Bragg coherent diffraction imaging (BCDI) have been applied since late in the 1990s to obtain 3D images of nanomaterials, also giving information of lattice strain and defects. BCDI consists in imaging single nanocrystals using highly coherent and very intense x-ray beams, demanding the use of very powerful light sources. The use of phase retrieval algorithms allows to reconstruct three dimensional images of single particles from diffraction patterns.

Some examples of applications of BCDI to electrochemistry, and other fields relevant to the area, comprise very important contributions to the study of batteries[1] and the behavior of nanomaterials[2]. Figure 1 shows an outstanding result in the field of heterogenous catalysis[3]. Through the 3D image of a Pt NP and measuring the lattice displacement, the authors were able to follow the chemisorption of CH_4 and O_2 on the NP. It is worth noting that similar experiments are still missing in the field of electrocatalysis.

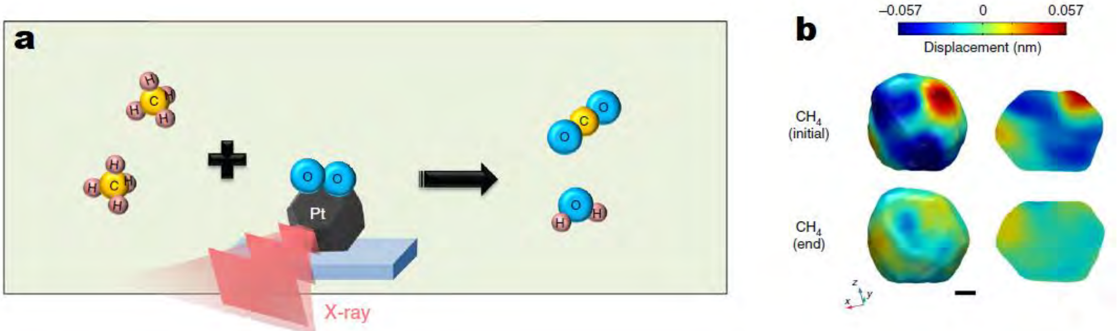

Figure 1. a) Scheme of *in situ* BCDI during methane catalytic oxidation. b) Displacement and 3D reconstructed of a 220 nm Pt nanocrystal during CH_4 oxidation. Red (positive sign) indicates the projected displacements along the [111] direction and blue (negative sign) implies the opposite direction. These 3D images show lattice contraction along the edges and corners owing to adsorption of oxygen atoms and methane. The cross-sections show that the distortion propagates deep into the interior of the Pt nanocrystal and is released after catalytic methane oxidation. The image was adapted from the literature[3].

In this work, we will summarize the most relevant advances of this technique applied to different electrochemical systems, including some interesting results recently reported at MAX IV[4], and we will also discuss about the future challenges that this technique must overcome to perform in situ/operando electrochemical experiments.

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Iron-doped Calcium Titanate as co-catalyst for the Oxygen Reduction Reaction (ORR)

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For sustainable economic growth and environment protection, energies generated from renewable sources result indispensable. In this field, polymer electrolyte membrane fuel cells (PEMFCs) are considered as a key element in the future clean energy becoming a promising solution. However, these devices present two major drawbacks, high cost and low durability that must to be solved for a their large scale application and commercialization. One main challenge concerns the development of highly stable reversible electrodes capable to catalyze efficiently the oxygen reduction reaction (ORR)[1,2]. Unfortunately, this reaction is kinetically sluggish toward electrons transfer because it is thermodynamically unfavorable, resulting in high overpotentials at the fuel cell cathode. Considerable efforts, in the last decade, were addressed to improve the electrochemical oxygen reduction reaction and to reduce Pt loading in order to achieve low-cost targets.

To this purpose, we here propose a study based on the use of a non-stoichiometric perovskite iron-doped calcium titanate ($CaTi_{0.8}Fe_{0.2}O_{3-\delta}$, CTFO) as co-catalyst for the oxygen reduction reaction (ORR).

Physical chemical investigations for the understanding of functional features of the proposed materials will be presented, such as the X-ray analysis of the perovskite reported in Figure 1.

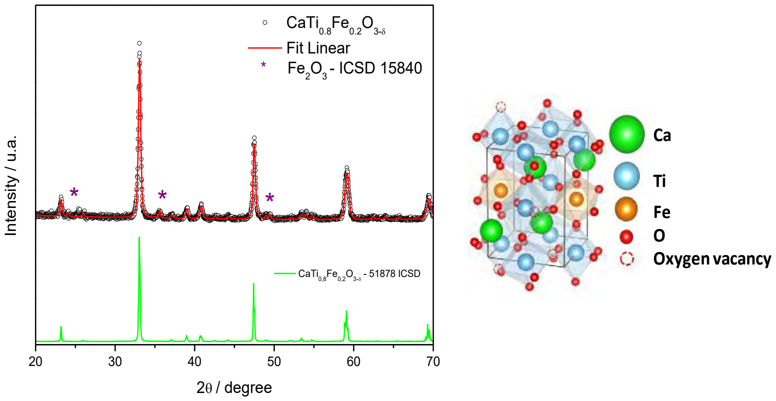

Figure 1: X-ray diffraction pattern of the synthesized $CaTi_{0,8}Fe_{0,2}O_{3-\delta}$ powder and its structure

Composite Pt/C electrodes, with different amounts of $CaTi_{0.8}Fe_{0.2}O_{3-\delta}$, were prepared and their catalytic performances were investigated by rotating-disk electrode (RDE) techniques. Two composite catalysts were prepared, Pt/C:CTFO 1:0,5 and Pt/C:CTFO 1:1 and compared with a commercial Pt/C catalyst used as reference. RDE measurements, have shown that the catalyst Pt/C:CTFO 1:1 posses the best activity toward the ORR presenting a 4 e-reduction pathway and exhibiting the most high limiting current density than the other samples. It is clear that the right amount of this perovskite can alter the ORR mechanism from 2e- pathway to a 4e- pathway, in fact a poor amount of additive seem to be not sufficient to improve the Pt/C catalytic activity.

By this preliminary study about the physical chemical and electrochemical properties of CTFO, we have demonstrated that this iron-doped perovskite is a promising electroactive material to be used as cathode catalyst support for low temperature fuel cells.

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Mathematical modeling of diffusion and convection in MEMS electroplating for energy and sensor technologies

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Advanced energy and sensor technologies require microelectromechanical systems with increased device performance, versatility, and efficiency. To enable this, 3D micro and nanoconductors have emerged as essential components for the miniaturization of next generation devices. Ubiquitous in the semiconductor industry, electroplating in wafer-scale lithography molds is a high-throughput fabrication method for micro and nanoconductive components. This work investigates methods to tailor the topology of electroplated 3D conductive components, such as electrodes, using CAD modeling in COMSOL Multiphysics. This enables meeting the design specifications of flat, convex, or concave substrate-distal electroactive surfaces. Flat conductor surfaces are ideal for microbump soldering and flip-chip fabrication methods and concave/convex designs increase the number of available electrode reaction sites for sensor applications. Coupled and uncoupled physics simulations were performed comprising laminar flow of a Newtonion fluid, the standard convection protocol for electrochemical baths, and electrochemistry modeling with the Nernst-Planck and Butler-Volmer formulations for mass transfer and reaction kinetics, respectively. Laminar flow or convection dominant electroplating conditions were found to create convex substrate-distal conductor topologies. Diffusion dominant electroplating conditions resulted in concave formations. Both effects can be coupled together to create a flat substrate-distal conductor topology. Simulation results are compared to directly corresponding experimental work, with positive correlation. By use of virtual mathematical modeling tools, such as COMSOL Multiphysics, crucial insights into the electroplating process can be gained. Herein, the phenomenon of substrate-distal electroactive surface topology is investigated with regards to the interplay between convection and diffusion dominant conditions. Our findings enable tailored and scalable surface topology processing options, which can be readily integrated into pre-existing research and industry standard operating procedures.

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Carbon-supported Cu/SnO$_2$ Core-shell Nanoparticles for the Selective Electrochemical CO$_2$ Reduction Towards Formic Acid

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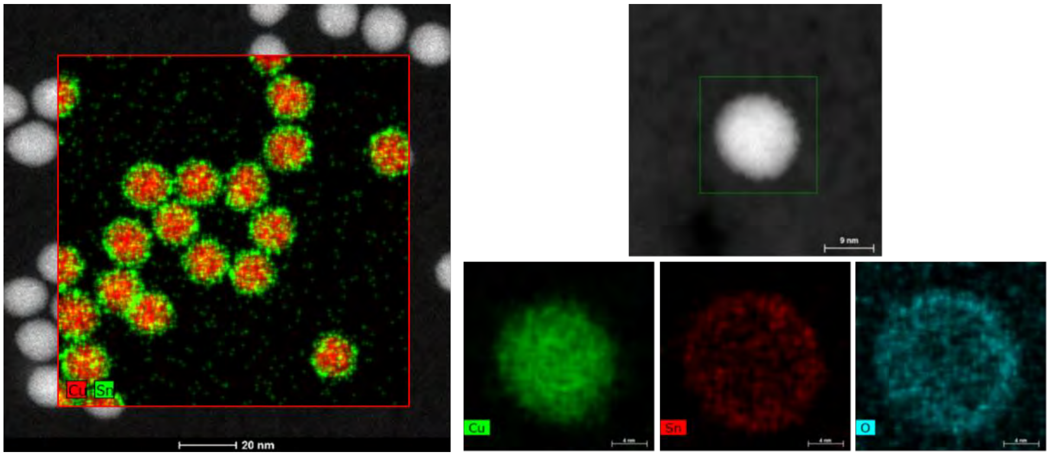
Increased levels of CO$_2$ in the earth's atmosphere, originating from excessive anthropogenic greenhouse gas emissions, are believed to be the main cause of global warming [1]. The electrochemical CO$_2$ reduction, however, provides a viable option for reducing anthropogenic CO$_2$ emissions, while at the same time closing the carbon cycle, by selectively converting CO$_2$ to for example formic acid. Formic acid is a valuable commodity chemical, not only because of its application in several chemical processes, such as textiles, pharmaceuticals and food chemicals, but also because of its potential as a hydrogen carrier [2].

Over the last decade, the electrochemical reduction of carbon dioxide towards formic acid has been studied extensively and several promising Cu/Sn electrocatalysts have already been reported [3]. Despite the reported high Faradaic efficiencies, the stability and activity of these state-of-the-art electrocatalysts and the contribution of the supporting material remains insufficiently studied.

In this work, we investigate the influence of the carbon support on the stability, current density (activity) and Faradaic efficiency, during the electrochemical reduction of CO$_2$ towards formic acid. This is done by comparing the performance of both unsupported- and carbon-supported Cu/SnO$_2$ core-shell electrocatalysts for the CO$_2$ reduction, through multiple chronoamperometric measurements, as this allows ranking the electrocatalysts with respect to their selectivity in function of applied potential. Furthermore, these catalysts were evaluated at industrially relevant conditions, in our in-house designed electrolyzer, revealing a good stability compared to literature. The supporting material is believed to play a key role in the enhancement of the stability and activity of our Cu/SnO$_2$ core-shell electrocatalysts.



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Effect of Interparticle Porosity and Electrode Thickness on the Desalination Performance by Capacitive Deionization

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Capacitive deionization (CDI) emerged as an energy-efficient desalination technology, in which ions are removed from the water and stored in the electrical double layer inside the pores of an activated carbon material. In this work, we demonstrated a comprehensive and systematic study of polyaniline activated carbon (PAC) electrodes prepared by blade-casting (DB) and free-standing (FS) techniques in order to enhance the salt adsorption capacity (SAC) and adsorption/desorption kinetics of the CDI process. The effects of interparticle porosity and electrode thickness on the textural and electrochemical properties of electrodes enabled a better understanding of how tuning the preparation technique of the CDI electrodes can improve the desalination performance. Although the different electrodes performed similarly in terms of gravimetric salt adsorption capacities, FS electrodes outperformed the DB electrodes in terms of volumetric salt adsorption capacities, because the carbon films were more compact and a large quantity of electroactive material was available for salt adsorption. In this case, a higher amount of salt can be removed using small CDI units equipped with FS electrodes. On the other hand, when the electrosorption and desorption kinetics are considered, the DB electrode presented superior performance due to its higher interparticle porosity that provides faster mass transfer in voids, thus increasing the ions transport to the PAC surface and the electrosorption rate. In this case, the DB electrode displayed the best performance for CDI applications involving aqueous diluted salt electrolytes. In summary, the presence of large interparticle porosity in thin thickness electrodes is important to obtain superior performance in the CDI process.

Copper hexacyanoferrate obtained from a nanocomposite between reduced graphene oxide and copper oxide nanoparticles for application in batteries

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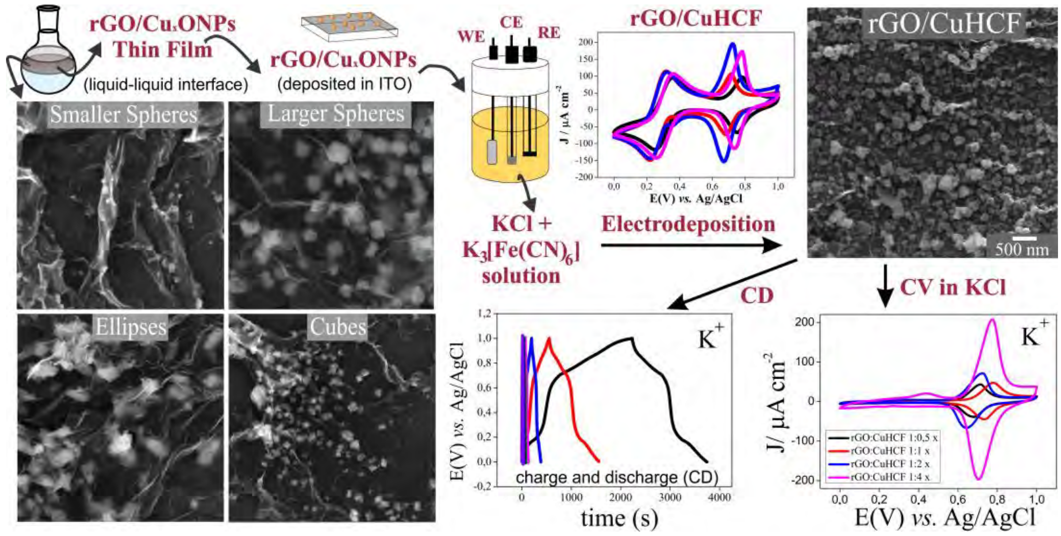
Prussian blue (PB) is one of the most studied mixed-valence materials and has become a class of compounds useful for large-scale metal-ion batteries, and its structure allows modifications that lead to a series of compounds, the so-called Prussian blue analogs (PBAs).[1] Among all PBAs, copper hexacyanoferrate (CuHCF) has unique characteristics, which can present reversible redox reactions in various supporting electrolytes containing Li^+, Na^+, NH_4^+, K^+, among others. Obtaining nanocomposites between PBA and carbon nanostructures improves some PBA characteristics, increasing both the electronic conductivity and the electrochemical stability. Several studies have demonstrated the potential of these nanocomposites as active materials to be used in batteries and capacitors, in which the charge and discharge processes are fast and reversible, showing high charge densities.[2] In this work we present a new route to obtain nanocomposite thin films between copper oxide nanoparticles (Cu_xONPs) and reduced graphene oxide (rGO) through a liquid-liquid interfacial reaction developed in our research group.[3] Twenty different films between Cu_xONPs and reduced graphene oxide (rGO) was obtained varying the ratio between the components. The precursors of the rGO/Cu_xONPs nanocomposite were reduced simultaneously and formed a self-sufficient thin film at the interface of the biphasic system. These films were deposited on different substrates and characterized by different techniques. The morphology of the copper oxide nanoparticles obtained from these materials varied in each sample, in relation to shape and size: smaller spheres (57 nm), larger spheres (179 nm), cubes (120 nm) and ellipses (200 nm) . Through X-ray diffractometry, it was possible to verify that the smaller spheres are Cu_2O species and the other morphologies were attributed to CuO, where most of these films are formed by mixtures between these species. After characterization, some films were used as precursors for the formation of nanocomposites between rGO and CuHCF, through an electrochemical reaction with $K_3[Fe(CN)_6]$ solution. After a systematic study the optimal condition to the electrodeposition was fixed in pH 2, potential range from 0.0 to 1.0 V (vs Ag/AgCl) and scanning speed of 20 mV s^{-1}. The best rGO/CuHCF film obtained was studied as a potential material for cathodes of aqueous metal-ion batteries. This film was evaluated for three different electrolytes (NaCl, KCl and LiCl) in the charge and discharge curves and different current densities (0.05; 0.10; 0.25; 0.50; 0.75; 1.00 and 2.00 A g^{-1}), where the best results were for Na^+ and K^+ reaching a capacity of 25 mA h g^{-1} at a rate of 0.05 A g^{-1}. The summary of this work is represented in the figure below.[4]



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Atomic Layer Deposition of IrO_2 and NiO thin films as anodes in Alkaline Water Electrolysis

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Recent studies show that the application of thin film materials to catalytic systems has begun to attract much attention, and the capacity to deposit these catalytic films in a highly controlled manner continues to gain importance. Atomic layer deposition (ALD) which is a special type of chemical vapor deposition (CVD) technique, is considered as one of the most attractive thin film deposition techniques where the conformality, uniformity, and thickness controllability of the films are crucial [1].

In this work [2], iridium dioxide (IrO_2) and nickel oxide (NiO) thin films (approximately 25 to 60 nm) were deposited on Ni expanded mesh suitable for industrial applications and on an Si (100) substrate, which served as a reference material. Subsequently, thin films deposited on Ni-expanded meshes were applied as anodes for alkaline water electrolysis. The choice of these two materials comes from the need to demonstrate the electrochemical activity of thin films for what are known to be particularly active noble and non-noble metal oxides for oxygen evolution reaction. Various ALD operating parameters (i.e., total number of deposition cycles, sublimation and deposition temperatures, and precursors pulse and purge lengths) were varied to determine their effects on the structure and the electrochemical performance of the thin film materials. With the requirement to run the electrolysis system at the lowest power consumption as possible for industrial applications and the next generation alkaline water electrolysis will operate at current loads around 1000 mA cm^{-2} (10 kA m^{-2}), the focus of this study is to compare the oxygen overpotential at such high current density. Results from the electrochemical tests (6 M KOH, 80 C, continuous agitation) showed the catalytic activity of the samples. Oxygen overpotential values were 20 to 60 mV lower than the uncoated Ni expanded mesh. In summary, the study has demonstrated the feasibility of using the ALD technique to deposit uniformed and electroactive thin films on industrial metallic substrates as anodes for alkaline water electrolysis.

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Electrochemical Conversion of Furfural, a Biobased Compound, in Unconventional Electrolytes

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Unconventional media like Room Temperature Ionic Liquids (RTILs) and Deep Eutectic Solvents (DES) are promising electrolytes for the electrochemical valorisation of biobased compounds. Indeed, their ability to solubilize lignocellulose and its by-products[1], their low vapour pressure and their large electrochemical window are particularly attractive. In addition, DES are inexpensive, easy to produce and environmentally friendly.

In this work, the ILs [BMPyrr][NTf_2] and [BMIm][NTf_2] and the DES Choline Chloride-Urea (ChCl-U) and Choline Chloride-Glycerol (ChCl-Gly) were used for the electroconversion of furfural (FF), a molecule extracted from hemicellulose. FF can be obtained in large quantities from agricultural waste like sugar cane bagasse, wheat straw or corn stover[1] and is a promising building block for the chemical industry[2].

NMR measurements after long-term electrolyses and in-situ FTIR coupled with electrochemical techniques were used to study the FF behaviour in these media.

In [BMPyrr][NTf_2], the reduction of FF leads to the formation of furfuryl alcohol, meso-hydrofuroin and d,l-hydrofuroin after electrolysis irrespective of the electrode material tested (Au, Pt, Cu, Ag, C). At carbon electrode, the electrochemical window is large enough to observe the oxidation of FF, tough electrolyses showed a blockage of the electrode resulting from adsorption processes.

In [BMIm][NTf_2], a single product, furoin, is observed after reduction at a gold electrode. The presence of carbene evidenced by NMR measurements supports an N-heterocyclic carbene catalysis mechanism for the formation of furoin.

In ChCl-U at 25°C, the degradation of FF by a condensation reaction between urea and FF was evidenced by NMR measurements and this medium was thus discarded. By contrast, FF showed to be stable in ChCl-Gly.

In ChCl-Gly, reduction of FF and formation of furfuryl alcohol were detected by the combination of in-situ FTIR and electrochemical techniques at gold and copper electrodes. The electrochemical stability of the DES itself was monitored by the same techniques. Degradation of the DES appears to be less significative on copper in comparison with gold. The electrochemical activity of synthesised Au/C and Cu/C nanoparticles for FF reduction was compared with the bulk materials.

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The phenanthro[9,10-*d*]imidazole framework as a new mediator platform for photo- and electrochemistry

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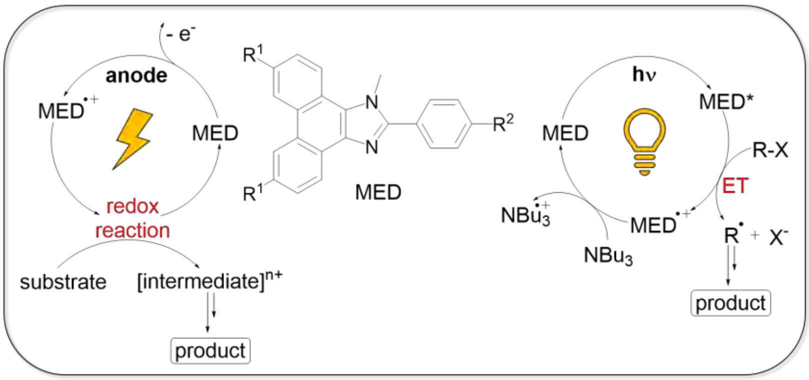
Redox mediators are often used in electro- and photochemistry to enable reactions that are otherwise not feasible or very slow.[1] For a long time, researchers in both fields have independently developed their own systems based on the individual requirements. Herein we present a new organocatalyst platform based on the phenanthro[9,10-*d*]imidazole structure (MED, see figure below), which can be used both for electro- and photochemical applications.[2],[3] Moreover, the mediator properties can be flexibly tuned by variation of R^1 and R^2.



Anodic oxidation of MED leads to formation of a radical cation, which can act as a single electron acceptor toward a substrate in solution and thereby trigger synthetically useful reaction sequences.[2] On the other hand, photoexcitation by blue light leads to an excited state MED* that can act as a strong reductant. MED* is capable of performing reductive dehalogenations leading to radical intermediates that can be used for C-C bond forming reactions.[4]

The properties of MED were investigated using cyclic voltammetry, preparative scale electrolysis, UV-Vis spectroscopy, fluorescence quenching studies and photochemical test reactions. In the present contribution, the results of these studies will be presented, including a comparison between the photo- and electrochemical applications and the influence of the substitution pattern on key-properties such as redox potential, light absorption and reactivity.

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Electrochemiluminescence microscopy boosted by nanotechnologies

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Electrochemiluminescence is a luminescent emission induced by an electrochemical stimulus. In the last decades, ECL emerged as a powerful analytical technique in many fields, like clinical assay and bioanalysis, thanks to the unique signal-to-noise ratio and spatial control of the emission [1].

The ECL intrinsic spatial resolution is crucial in the combination with microscopy, an emerging approach for the visualization of micro and nano-metric objects and biological materials in close proximity to the electrode surface. ECL microscopy applications and features are being deeply studied for increase the sensitivity and the successful surface-confined mapping of analytes [2]. In the quest for reaching these goals, ECL microscopy can be coupled to nanotechnologies.

Nanomaterials, such as nanoparticles and carbon nanotubes (CNT), are being widely studied in combination with ECL for enhancing the analytical signal [3]. Herein, nanomaterials will be used for extending the spatial emission of ECL imaging, which is normally confined in close proximity to the electrode surface (distance < 3 μm). CNTs or graphene, thanks to their highly conductivity, were used to create a sort of conductive layer all around labelled objects [4]. Here we demonstrated that ECL emission active area is extended with a consequent enhance in the ECL signal. This novel approach has been applied to beads with different dimension (ranging from 1 to 4 μm) providing novel insights into the mechanisms underlying ECL generation.

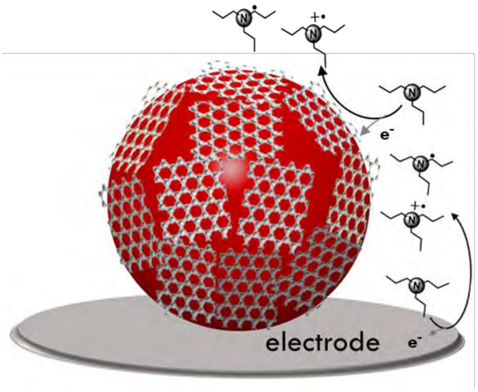

Figure 1: Generation of a conductive layer for ECL signal enhancement

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New Ways for Heat Energy Conversion: Eu(III)/Eu(II) Redox Couple in Ionic Liquids

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Due to technological progress and population growth, a huge increase in demand for energy is expected in the next years. However, energy production and consumption are accompanied by significant heat losses which generate a direct nuisance on the environment and contribute to climate change. One of the promising routes to new energy resources is the use of this waste heat. In such a context, an interesting way for the direct conversion of low grade heat into electricity is the use of thermogalvanic cells (TGCs) containing ionic liquids (ILs) as electrolyte [1, 2].

Our choice of the system was focused on the solutions of europium in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIM.TFSI). The apparent standard potential of the redox couple Eu(III)/Eu(II) strongly depends on the temperature in various ILs based on the anion $TFSI^-$ [3], our objective was therefore to explain this phenomenon and to develop new TGCs. We studied the properties of the solutions of europium(III) and (II) as a function of temperature and in the presence of various ligands (water, dimethylsulfoxide, dimethylacetamide, bromides, etc.) by numerous spectral and electrochemical methods.

Cyclic voltammetry study has shown that electroreduction of europium(III) species is irreversible in an anhydrous medium on a glassy carbon electrode. However, the redox process becomes quasi-reversible after the addition of ligands or the temperature increase. In particular, we studied the competitive complexation of europium(III) ions by water and $TFSI^-$ or Br^- anions over a wide range of temperatures. The diffusion coefficients of the europium(III) species were of the order of 10^{-7} $cm^2.s^{-1}$ at 61.5 ° C. In our work, we have shown that the Seebeck coefficient can reach a record value of -5.5 $mV.K^{-1}$ due to the competitive complexation of europium ions in ionic liquid medium.

The new TGCs were tested under open and closed circuit conditions, and the obtained data were in perfect agreement with the results of cyclic voltammetry. The electrical power measurements were carried out and the optimization work is underway.

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Nickel Catalyst Migration in Anion Exchange Membrane Fuel Cells

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Nickel materials have been widely studied as non-platinum group metal (non-PGM) cathode catalysts for anion exchange membrane fuel cells (AEMFC). Although the stabilities of many Ni catalysts have been tested by accelerated potential cycling, the studies do not fully simulate the operating Anion Exchange Membrane Fuel Cell (AEMFC) conditions. For back-up power systems, the standby AEMFCs are at a high steady state cell potential. For cathode catalysts, this is a more challenging condition than cycled potentials and the stability of Ni catalysts need to be re-examined.

Ni is stable in many alkaline electrochemical applications because of the formation of a NiO_x passivation film at the surface under water splitting potentials, which prevents further corrosion [1]. However, AEMFC operating conditions could disrupt the Ni passivation mechanism. According to the thermodynamic model by Beverskog et al., Ni formation of $Ni(OH)_3^-$ ([I]= 10^{-8} M) is possible when the pH > 11 and the potential is within 0.1V-1.0V vs. RHE potential, which covers the range of AEMFC operating conditions [2]. This suggests that, especially with high cathodic AEMFC potentials, Ni, including both Ni metal and Ni oxides, may potentially dissolve to form $Ni(OH)_3^-$. This could cause a significant challenge to the known Ni passivation mechanism as the surface NiO_x protection film may dissolve to form mobile ions leaving the underlying Ni susceptible to corrosion. Especially when the AEMFC is operating at a constant high voltage at standby, the steady state cathode potential could keep the Ni species dissolved and allow the mobile Ni species migrate to other AEMFC components, which could be detrimental to fuel cells,

This study was aimed at examining the stability of Ni at an AEMFC cathode, under steady state cell potentials. A basic Ni composite catalyst, Ni on Vulcan® XC72 carbon (Ni/C), was used as the catalyst to research cathodic Ni behavior under the study conditions in a simulated AEMFC with constant oxygen flow. A steady state potential of 0.9V was held across the cell for 1500 hours of testing. The resulting changes in Ni morphology due to dissolution and migration were significant and were examined at multiple cell locations, using scanning electron microscopy (SEM), scanning transmitted electron microscopy (STEM), and X-ray Photoelectron Spectroscopy (XPS) analysis. These analyses on Ni migration should provide a benchmark for the use of Ni catalysts in AEMFC.

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Proton Insertion Chemistry of a Zinc-Organic Battery

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Rechargeable aqueous zinc-ion batteries (ZIBs) are attracting more attention since the Zn anode possesses low redox potential (-0.76 V *vs.* standard hydrogen electrode (SHE)), high specific capacity (820 mAh g^{-1}), excellent stability in water and low cost.[1] The electrochemical performance of ZIBs mainly depends on the design of cathode materials. Recently, various active materials such as transition metal oxides or sulfides (based on vanadium[2] and manganese[3]), Prussian blue analogues[4] and organic compounds[5] were developed to serve as the cathode materials of aqueous ZIBs. Among them, organic materials are considered as a promising candidate because of their renewability, environmental friendliness, low cost and structural diversity.

The proton storage in rechargeable aqueous zinc-ion batteries (ZIBs) is attracting extensive attention due to the fast kinetics of H^+ insertion/extraction.[6] However, up to now, it is not achieved in organic materials-based ZIBs with a mild electrolyte. Herein, we developed aqueous ZIBs based on diquinoxalino [2,3-*a*:2',3'-*c*] phenazine (HATN) in a mild electrolyte. Electrochemical and structural analysis confirm for the first time that such Zn/HATN batteries experience a H^+ uptake/removal behavior with highly reversible structural evolution of HATN. The H^+ uptake/removal endows the Zn/HATN batteries with enhanced electrochemical performance. Proton insertion chemistry will broaden the horizons of aqueous Zn/organic batteries and open up new opportunities to construct high-performance ZIBs.

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Nanostructured Palladium Electrocatalyst Supported on MOF-Derived Carbon for Alkaline Water-Splitting Reactions

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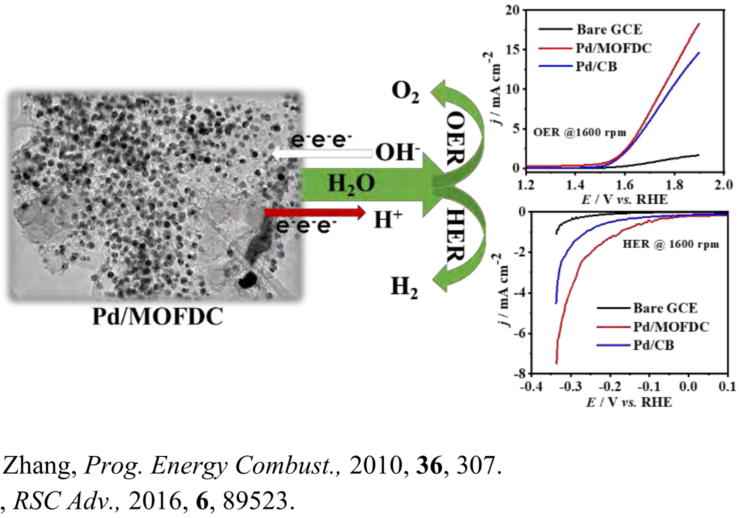
The hydrogen economy is one of the strategies to phasing out fossil fuel technology in the core sustainable development goal (SDG 7) where hydrogen (H_2) is generated from water and employed as fuel for clean and renewable energy. Alkaline water electrolysis has long histories and presently used in industries for H_2 production using platinum (Pt) catalysts.[1] However, the Pt is scarce and poor electrocatalytic activity in alkaline conditions compared to palladium (Pd) electrocatalysts.[2] This informed the interest to design a novel nanostructured Pd electrocatalyst on metal-organic framework (MOF)-derived carbon support. The MOF is used as a sacrificial template because of its interesting properties which are inherited in the derived carbon.[3] This work studies the cobalt-based MOF-derived carbons (MOFDC) as new carbon-based support for Pd catalyst for electrochemical water-splitting; i.e., hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline medium. The study shows a high increase in the HER activity, in terms of low onset overpotential (onset η = 35 mV *vs.* RHE), high exchange current density ($j_{o,s} \approx 0.22$ mA cm^{-2}), high mass activity ($j_{o,m} \approx 59$ mA mg^{-1}), high kinetic current ($j_K \approx 5 - 8$ mA cm^{-2}) and heterogeneous rate constant ($k^0 \approx 4 \times 10^{-4}$ cm s^{-1}) are attributed to the high porosity of the MOFDC and contribution from Co residue, while the large Tafel slope (b_c = 261 mV dec^{-1}) is ascribed to the high hydrogen adsorption onto the polycrystalline Pd as supplementary reaction step to the suggestive Volmer–Heyrovsky mechanism. These values obtained for the catalyst are comparable or better than many recent reports that adopted nano-carbon materials and /or use bi- or ternary Pd-based electrocatalysts for HER. The improved HER activity of the Pd/MOFDC is associated with the positive impact of MOFDC and Co residue on the Pd catalyst (i.e., low activation energy, $E_A \approx 12$ kJ mol^{-1}) which allows for easy desorption of the H_{ads} to generate hydrogen. Moreover, the Pd/MOFDC displays satisfactory OER activity than its analogue, with lower onset η (1.29 V *vs.* RHE) and b_a ($\approx$ 78 mV dec^{-1}), and higher current response (ca. 18 mA cm^{-2}). Indeed, this study provides a new strategy of designing and synthesizing MOFDC with physico-chemical features for Pd-based electrocatalysts that will allow for efficient electrochemical water-splitting processes.

Graphical Abstract



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Bipolar Electrochemical Exfoliation of Graphite for the Production of Oxygen Reduction Reaction Electrocatalysts

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Few-layer graphene structures (FLGS) doped with heteroatoms (N, P, S and B) and/or their nanocomposites with transition metals oxides demonstrate distinct catalytic activity towards the oxygen reduction reaction (ORR). Such materials are considered as promising candidates to replace platinum-based catalysts in the cathodes of fuel cells and metal-air batteries [1]. Recently, the usage of electrochemical methods for the synthesis of few-layer graphene structures (FLGS) has become increasingly popular. At current densities greater than 20 $A \cdot cm^{-2}$, high-voltage impulses applied to the graphite electrodes immersed into electrolyte solution lead to the formation of electrolytic plasma [2,3]. A certain advantage of plasma-assisted electrochemical exfoliation of graphite is the diversity of modes of carbon nanostructures synthesis.

In the present study, a bipolar electrochemistry approach was utilized to realize an electrochemical exfoliation of graphite in two separate electrochemical cells. A “closed” circuit was implemented in which a bipolar electrode (BPE) was located in the completely separated cathodic and anodic compartments and voltage pulses were applied to the driving electrodes with a significantly larger surface area compared to that of BPE. The process was carried out using the set-up designed in the laboratory of laser electrochemistry of IPCP RAS [3] in the mode of alternating anodic-cathodic plasma. Each cell contained a different electrolyte, namely 1 M Na_2SO_4 and 1 M Na_2SO_4 + 0.01 M $MnSO_4$ were used. As a result, FLGS were synthesized in the first cell and nanocomposite of FLGS with manganese oxides were produced in the second one. Materials obtained in this way were characterized in detail using elemental analysis, scanning electron microscopy and X-ray photoelectron spectroscopy. Besides, oxygen reduction reaction was studied by the rotating disk electrode method at individual electrocatalysts and their mixture as well. Based on the obtained data, it can be concluded, that the usage of solution containing manganese salts allows one to produce FLGS nanocomposites with Mn_3O_4 which demonstrate high electrocatalytic activity towards the oxygen reduction reaction.

Thus, these results indicate the possibility of production of active platinum-free ORR electrocatalysts based on the nanocomposites of carbon nanostructures with transition metal oxides in the course of electrochemical exfoliation of graphite in the mode of electrolytic plasma realized in a bipolar configuration.

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A Chemically Self-Charging Aqueous Zinc-Ion Battery

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Rechargeable batteries are widely used in many fields such as electric devices and grid-scale energy storage systems. In general, the commercial batteries are often charged by electrical grid. However, in the harsh environment or remote area, the electrical grid is unavailable, which limits the recharging and reuse of batteries. In order to solve this issue, various energy harvesting technologies, such as photovoltaic devices, piezoelectric nanogenerators, triboelectric nanogenerators and thermoelectrics, were integrated with batteries into self-charging power systems. However, the conventional integrated systems are highly dependent on the availability of the energy sources and generally possess complicated configuration. Herein, we develop chemically self-charging aqueous zinc-ion batteries with a simplified two-electrode configuration based on $CaV_6O_{16}{\cdot}3H_2O$ electrode. Such system possesses the capability of energy harvesting, conversion and storage simultaneously. It can be chemically self-recharged by the spontaneous redox reaction between the discharged cathode and oxygen from the ambient environment without any external power supply. Chemically self-recharged zinc-ion batteries display an initial open-circuit voltage of about 1.05 V and a considerable discharge capacity of about 239 mAh g^{-1}, indicating the excellent self-rechargeability. Impressively, such chemically self-charging zinc-ion batteries can also work well at chemical or/and galvanostatic charging hybrid modes. This work not only provides a route to design chemically self-charging energy storage, but also broadens the horizons of aqueous zinc-ion batteries.

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Engineering Active Sites of Polyaniline for $AlCl_2^+$ Storage in Aluminum-ion Battery

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Rechargeable aluminum-ion batteries (AIBs) have poured tremendous attention as energy storage devices due to its impressive advantages such as low cost, high safety, and environmental benignity.[1] Furthermore, aluminum is the most abundant metal in the earth's crust and possesses three-electron redox reaction characteristics. As a result, Al metal achieves an excellent gravimetric capacity of 2980 mAh g^{-1}, and a high volumetric capacity of 8040 mAh cm^{-3}.[2] Additionally, aluminum metal electrode is stable in air under ambient condition, which is convenient for manufacturing as compared to other active alkali metals. Therefore, AIBs are considered as a promising candidate of energy storage devices.

The reversible capacity of $AlCl_4^-$ intercalation/de-intercalation in conventional cathodes of aluminum-ion batteries (AIBs) is often difficult to be improved due to the large size of $AlCl_4^-$ anions. Therefore, it is highly desired to realize the intercalation/de-intercalation of other Al-based ions with smaller size.[3,4] Here, we fabricated polyaniline/single-walled carbon nanotubes (PANI/SWCNTs) composite films and further protonated the PANI nanorods in them. The protonation endows PANI with more active sites and enhanced conductivity. More importantly, hyper self-protonated PANI (PANI(H^+)) exhibits the reversible $AlCl_2^+$ intercalation/de-intercalation during discharge/charge process. As a result, the Al/PANI(H^+) battery displays a twice higher discharge capacity in comparison with the initial composite films. Furthermore, PANI(H^+)@SWCNTs electrodes also display stable cycling life with only 0.003% capacity decay per cycle over 8000 cycles. In addition, owing to the excellent mechanical properties, PANI(H^+)@SWCNT composite films can act as the electrodes of flexible AIBs. As a proof of concept, the flexible cable-type AIBs were assembled based on them and remained stable electrochemical performance at bending states. This work will pave the way for the applications of conducting polymers in AIBs and broadens the horizons of AIBs in flexible energy storage devices.

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Ru-doped perovskite as new electrode material for SOFCs

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Solid oxide fuel cells (SOFCs) have a great potential among the emerging energy conversion technologies because they can efficiently convert various types of fuels (hydrogen, methane, CO, biogas) into electrical energy in the temperature range 650-850 °C. The choice of electrodes remains a challenge because most of metal oxides suffer of low chemical stability and conductivity in reducing atmosphere and low electrocatalytic activity toward oxygen reduction reaction (ORR) in the intermediate temperature range [1]. In this view, perovskite oxides (ABO_3) have shown promising properties in terms of thermal stability, compatibility with other cell components, low production cost and, most importantly, great flexibility [1]. $La_{0.6}Sr_{0.4}FeO_{3-\delta}$, (LSF) perovskite oxide have been widely investigated for its high electrical conductivity and electrochemical properties [2]. However, the main drawback is the poor activity towards ORR in the intermediate temperature range (500-700 °C), as in the case of the most iron-based perovskites [3]. The B-site doping with metal catalysts can sensitively improve the properties and make the compounds suitable for electrodes application.

Ruthenium is a low-cost noble metal and a promising catalyst for hydrogen oxidation and methane reforming [4]. The addition of Ru into LSF structure can be an innovative approach to improve the electrocatalytic properties. Specifically, we synthesized B-site doped LSF powders with different mol % of Ru (2%, 5%, 10%) by using a solution combustion synthesis (SCS). The synthesized powders were calcined at quite low temperature (750 °C for 6h) to get as high as possible surface area (>15 m^2/g). All compounds show a single perovskite phase. As reported in Fig. 1 (a), the addition of Ru in the structure causes a progressive shift of the XRD peaks to lower 2θ angles indicating an expansion of the perovskite lattice due to the substitution of Fe^{3+} sites (0.645 Å) with larger Ru^{3+} ions (0.68 Å).

The compounds were investigated both in oxidizing and reducing conditions. Fig. 1(b) shows the Arrhenius plot of area specific resistance (ASR) values of LSFRu perovskite oxides in air. The ASR values were measured by electrochemical impedance spectroscopy (EIS) on LSFRu/$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM)/LSFRu symmetric cells in the temperature range 550-800 °C. By increasing Ru amount the activation energy is reduced, and, most importantly, the ASR values of LSFRu compounds are lower than that of LSF at T<700°C. These features suggest that Ru substitution positively affects the electrocatalytic and conductivity properties valuably for cathodic applications.

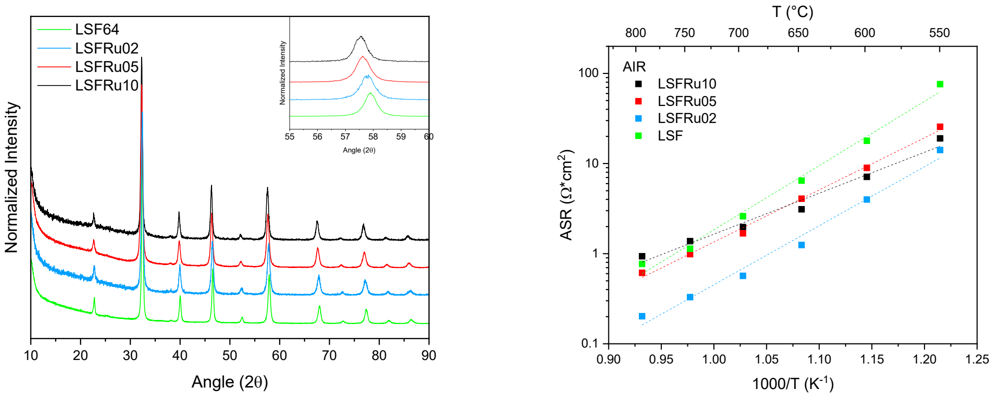

Figure 1. Structural and morphological characterization of LSFRu (a) XRD patterns (b) ASR values obtained in air flux (100 cm^3/min) from 800°C to 550°C

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Insights into the Electrochemical Degradation of Real Effluents Using Modulated Current

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In this work, we demonstrated the feasibility of using the modulated current (MC) technique, in which the applied current is maintained at the limiting current for energy minimization in the electrochemical mineralization of effluents from coffee processing using boron-doped diamond electrode [1]. Although the wet coffee processing reduces the costs with drying and provides a superior product quality, this process generates effluents containing high concentrations of phenolic compounds, among them the caffeic acid (CA). Prior electrolysis, the wastewater was filtered and acidified with H_2SO_4, which worked as supporting electrolyte to increase the conductivity. Due to the effluent complexity, a new criterion to establish the operational conditions for electrooxidation is presented, based on the total organic carbon (TOC) and the CA diffusion coefficient (k_m) to determine the limiting current (I_{lim}). It was demonstrated that a combination of the modulated and galvanostatic (CC) current control is more effective to remove TOC and phenolic compounds after 12 h of electrolysis. Using the combined MC+CC approach, the energy consumption diminished ~79.5% compared with fully galvanostatic procedure. Importantly, attention must also be paid to avoid performing the MC control at currents below the water discharge since electrode passivation may occur. A 100% mineralization current efficiency (MCE) was observed throughout the electrolysis of the wastewater, indicating that the process operated under activated control. This result suggests that the criterion used to calculate I_{lim} and modulate the applied current was not satisfactory to optimize the reaction rate since the I_{lim} was underestimated. In this case, the chemical oxygen demand seems to be a more reliable parameter to estimate k_m and I_{lim}, and an apparent kinetic constant including the contributions of mass transfer and bulk oxidants may be considered since industrial effluents are complex mixtures of organics and ions. After the wastewater electrolysis, the MCE and energy consumption were 99.1% and 30.5 kWh kg^{-1} TOC, respectively, leading to a treatment cost of 1 m^3 of the coffee processing wastewater estimated in US$ 4.39. In summary, the MC+CC technique is a simple and effective tool that reduces the energy costs of the electrochemical treatment of effluents containing organic pollutants.

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Characterisation and Application of Weakly Coordinating Solvents for the Electrodeposition of Semiconductors

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Compound semiconductors based upon p-block elements are receiving intensive research for their use in advanced electronic devices. The possible combination of elements is significant and contains ternary or quaternary alloys. This creates a broad range of properties and permits a diversity of applications.

Electrodeposition requires an electrolyte containing the metal precursors of interest. p-block complexes have particularly labile ligands. In a solvated metal complex the solvent molecules can compete for coordination to the metal cation. As such, a complex with labile ligands in a Lewis basic, coordinating solvent is vulnerable to displacement by the solvent molecule. Different metal cations will differ in their interaction with the solvent and therefore inconsistent speciation across metal precursors is possible. Metal speciation affects all aspects of an electron transfer reaction and so unpredictable speciation greatly complicates the process of codeposition. Hence, a plating bath composed of precursors sharing common ligands and a weakly coordinating solvent (WCS) is desirable.

We present results of a study into the feasibility of five organic solvents classified as weakly coordinating (the classification process being a part of the present investigation), shown in Fig. 1, for the electrodeposition of p-block elements. Additionally, dichloromethane is used as a control due to its previous demonstration as a suitable WCS for semiconductor electrodeposition.[1, 2] Firstly, the criteria of a suitable solvent, including the degree of coordination, are identified and quantified using Kamlet and Taft's solvent descriptors,[3] and it is established that solvents typically used in electrochemistry, such as water, acetonitrile or dimethylsulphoxide are not suitable (see Fig. 1). Several of the solvents have seen little use in electrochemistry and so their capability as electrochemical solvents is examined with measurements including conductivity, potential window and the electrochemistry of the model redox couples decamethylferrocene and cobaltocenium hexafluorophosphate. Subsequently, those solvents deemed suitable are applied to the electrodeposition of bismuth telluride and other novel systems.

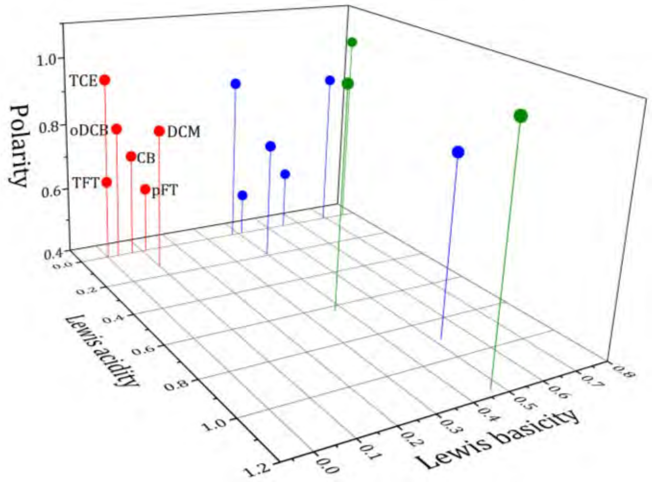

Figure 1: Kamlet and Taft parameters of red: candidate weakly coordinating solvents, blue: common electrochemical solvents, green: typical ionic liquids, from Ref. 4. DCM: dichloromethane, TFT: trifluorotoluene, oDCB: o-dichlorobenzene, pFT: p-fluorotoluene, CB: chlorobenzene, TCE: 1,1,2,2,-tetrachloroethane.

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The Impact Of Polymer Gel Electrolytes With Varying Transport Properties On Cycling Of Lithium Ion Battery Systems

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Advanced batteries will enable more widespread adoption of electric vehicles which, when charged with electricity generated from non-fossil fuel sources, can enable the achievement of global greenhouse gas emissions targets.

In LIB battery systems, the electrolyte has a crucial role in terms of allowing the transport of ionic charges and maintaining the physical isolation between anode and cathode. In commercial lithium ion batteries, dual-ion electrolytes such as $LiFP_6$ in organic solvent mixtures (EC/DEC or EC/DMC v/v=1:1) are commonly utilised. This type of electrolyte provides high ionic conductivity and has been widely in used commercial applications despite a couple of drawbacks.

Notwithstanding the high total ionic conductivity, common liquid Li-ion electrolytes have Li transference number lower than 0.5 [1]. The non-unity transference number of the active cation results in formation of a concentration gradient during charge/discharge. Accumulation of anions at the electrode-electrode interface and depletion of cations lead to increased interfacial impedance and reduced limiting currents. To overcome the drawbacks, polymer based electrolytes have been proposed, specifically, single ion conducting polymer and gel polymer electrolytes (SIPEs)[2], [3]. In SIPEs, the anion is fixed to polymer backbone to prevent its migration to the anode, which allows only Li^+ transport in the system. However, the low ionic conductivity of SIPEs has slowed their use in practical devices.

In this study, we report on the fabrication of crosslinked polymer gel electrolytes with varied nanostructures and containing both free salt and bound charge, via swelling of the network ionomers with liquid electrolyte solutions. We obtain a family of polymer gel electrolytes with varying lithium transference numbers (0.4 to 0.78) and total ionic conductivity ($2.71x10^{-4}$ S/cm to $1.93x10^{-3}$ S/cm). Interestingly, it is found that transference number and conductivity are not mutually exclusive and, for certain systems, an increase in the lithium transference number is not accompanied with a decrease in total ionic conductivity. It is also observed that the structure of the polymer has a great impact on transport properties. The effects of varying ion transport properties on Li-ion battery rate capability are investigated with the $Li/LiFePO_4$ configuration.

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DFT Study on Nitrogen Reduction Electrocatalysts Regulated by Hydrogen and p-Block Elements

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Electrocatalytic nitrogen reduction reaction (NRR) represents an alternative eco-friendly strategy for sustainable N_2 fixation with renewable electric energy.[1] However, the NRR suffers from sluggish kinetics due to difficult N_2 adsorption and triple N≡N cleavage. Mechanistic understanding of the reaction helps to exploit strategies for performance enhancement of the NRR electrocatalysis. Density functional theory (DFT) calculation has been widely used to explore the electronic structure of catalysts, active sites and reaction pathways. Recently, we reported experimental and DFT computation on nanoporous palladium hydride as efficient electrocatalyst for electrochemical N_2 reduction under ambient conditions.[2] We showed superior catalyst activity of nanoporous hydrogenated palladium (exemplified composition of np-$PdH_{0.43}$) to nanoporous palladium (np-Pd). The projected density of states (PDOS) indicated that the d band center of np-$PdH_{0.43}$ is closer to the Fermi level compared to np-Pd (-1.61 vs. -1.68 eV) due to the hybridization between Pd and H atoms, resulting in the stronger interaction between catalysts and intermediates. The difference of Gibbs free energy (ΔG) for the energy-determined first proton-coupled electron transfer step was calculated at different Pd atoms on np-$PdH_{0.43}$ to predict the active sites. Charge density difference images further revealed stronger charge redistribution at np-$PdH_{0.43}$, which promoted the accumulation of internal electron concentration and enhanced the electrocatalytic activity. Then, the Gibbs free energy profiles of NRR confirmed that the enzymatic NRR pathway was favorable compared with distal and alternating pathways for both np-Pd and np-$PdH_{0.43}$, and the *NNH formation was the rate-limiting step. In addition to hydrogen, using p-block elements such as antimony (Sb) was also found to be a promotor to fix nitrogen. Results of PDOS indicated that d band center of transition metals (TMs) can be regulated by electrons from p orbitals of neighboring Sb atoms. Analysis of charge density difference again suggested activation of N_2 by TMs-Sb due to the redistribution of surface charges. In this scenario, the hydrogen injection and p-block element alloying would effectively modify the d-electron domination of TMs, thus stabilizing the intermediates and boosting the NRR.

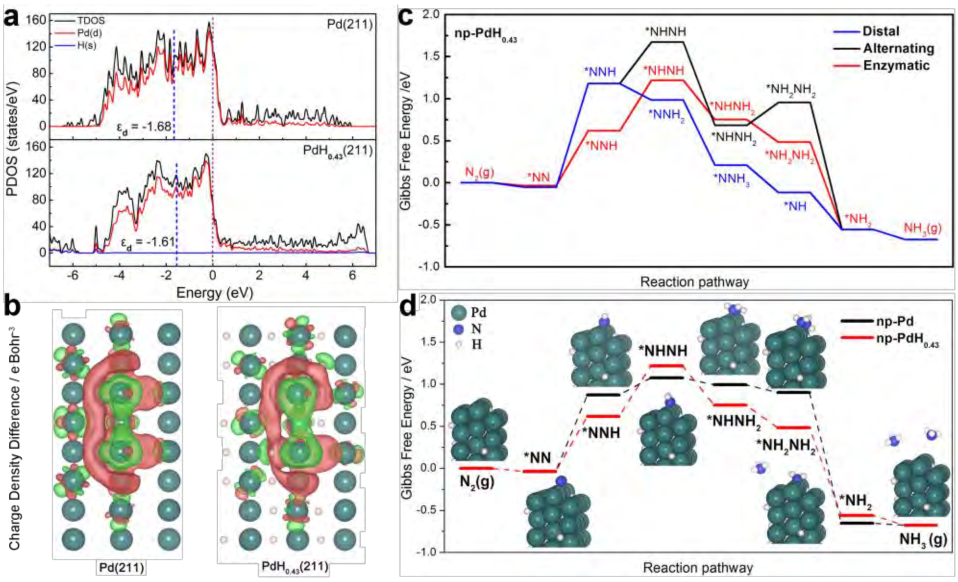

Figure1. (a) Projected density of states. (b) Charge density difference. (c, d) Gibbs free energy profiles of the NRR.

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Role of Additives on Tuning of the Electrochemical Roughening of Platinum

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Platinum is ~~thus~~ by far the most active catalyst for many electrochemical devices such as ~~e.g.~~ electrolysers. However, ~~this~~ platinum is not only scarce and expensive, it also ~~metal~~ suffers from degradation upon prolonged usage as an electrode. The surface roughens significant~~erious~~ly~~,~~ due to ~~The~~ the nucleation and growth of surprisingly well-ordered nanoislands ~~leads to surface roughening and this is known to be the responsible for its degradation~~ [1, 2, 3, 4]. Additives like chlori~~d~~n~~e~~ might offer a solution to decrease this roughening~~.,~~ H~~h~~owever ~~The~~ the effect of additives on this phenomenon is still fully unclear~~has been not studied in depths~~. ~~In this work, we study~~In this work, we study the platinum ~~deterioration~~ roughening in the presence of chloride ~~under potential cycling~~under potential control.~~during oxidation-reduction cycling.~~ We obtain quantitative information about the roughening process from the ~~with the presence of chloride, which is a very common contaminant in electrochemistry. The~~ evolution of the~~-~~ electrochemical signal~~step peaks/signal in the CVs~~. Although chloride has been~~having often been~~ identified as a~~n~~ diffusion enhanc~~inger agent~~ for many different surfaces~~ and metals~~, with platinum we surprisingly find a faster build-up of the roughness ~~in the presence of chlorine~~if chloride is present in solution [5]~~. [we could stop here…if we want…] Is chlorine now blocking the diffusion for platinum? It could also only accelerate the mass transport being responsible for the roughening. We will address this difficult question.~~

~~of the Pt(111) electrochemical signal with time conveys important information about this roughening process. We attribute the faster roughening with chloride to a higher flux of platinum atoms pushed out from the surface, before redepositing and giving shape to the nanoislands.~~
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~~Finally…..everything which is marked in yellow…..is pure for “selling” reasons hoping to attract people in this way….please realize!!!~~

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Synthesis and Electrochemical Characterization of 1D and 2D Coordination Polymers for Energy Storage Applications

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Coordination polymers (CPs) have attracted interest in recent years due to their properties such as gas adsorption, drug delivery, catalysis and ionic conductivity. CPs have advantages from its highly ordered and porous structure and a wide design latitude of compounds by choosing various metal ions and bridging ligands. In this communication, we will show a series of CPs ($\{[Fe(CA)(H_2O)_2]H_2O\}_n$ and $\{[Mn(CA)(H_2O)_2]H_2O\}_n$) [1] with one or two dimensionalities synthesized by environmentally friendly routes and low cost precursors. These CPs contain chloranilic acid, dihydroxybenzoquinone and pyrazine linkers combined with iron and manganese. These compounds were studied as electrode for lithium-ion batteries [2]. The lithium insertion potential changed depending on the metal used. This fact combined with the high voltages of reaction suggests the participation of both metal and organic linker on the redox processes (Fig. 1A). We also noticed that a thermal treatment on the CPs before the half-cell assembly was crucial to optimize the electrochemical performance of our compounds.

Furthermore since one of the Fe CPs showed two reversible redox stages at -0.5 and 0.5 V (Fig. 1B) it was studied as potential single electrolyte in redox flow batteries systems. Not all the CPs were suitable for the study, mainly due to the low stability of the suspension. However, by modifying the synthesis route, we manage to decrease the particle size and create slurries with high water-stability and study their electrochemical properties on a symmetrical cell.

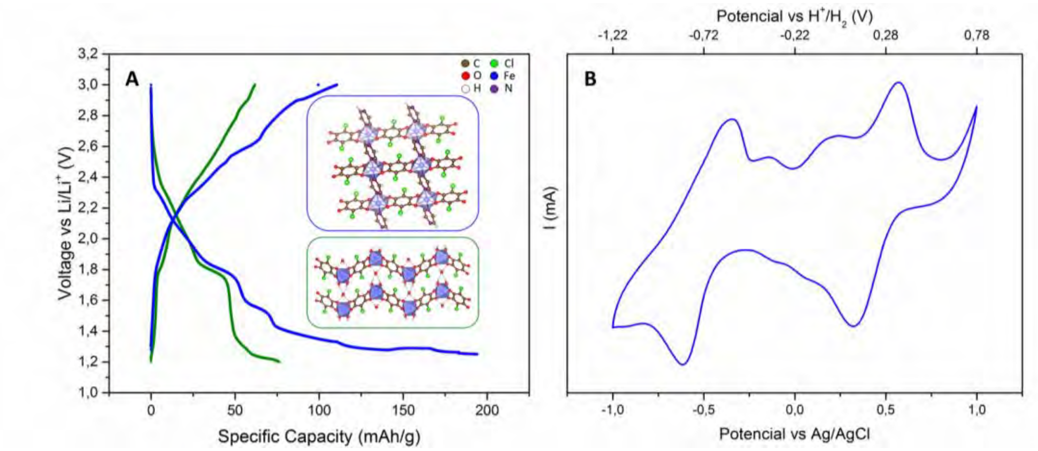

Figure 1. Galvanostatic charge-discharge cycling profile of two of the Fe CPs (A). Cyclic voltammetry of the Fe CP in an aqueous solution with 0.5 M NaCl at a current density of 20 mV/s (B).

Acknowledgements

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CuX and NiX Nanozeolites as Electrocatalysts for Alkaline Oxygen Evolution Reaction

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The electrochemical water splitting (EWS) is composed of oxygen evolution reaction (OER) as an anode process and hydrogen evolution reaction (HER) as a cathode process. Pure hydrogen fuel produced by EWS could be a promising replacement for fossil fuels because of significantly lower pollution during its use and high energy transformation rate [1]. Alkaline water electrolysis (AWS) and its half reactions, OER and HER in alkaline media are presented by **Eq. 1, 2** and **3**, respectively.

AWS: $2H_2O \rightarrow 2H_2\,(g) + O_2(g)$ (1)
OER: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ $E^0 = 0.404$ V vs. SHE (2)
HER: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ $E^0 = -0.826$ V vs. SHE (3)

The overall energy efficiency of AWS is largely obstructed by the slow OER kinetics as a four-electron process with the high energy expended for oxygen-oxygen bonding [2] and high overpotential needed to break it [1,3]. Therefore, it is of utter importance to find appropriate low-cost OER electrocatalyst which could improve OER kinetics with more energy saving. Noble metals such as platinum (Pt) and their oxides such as ruthenium and iridium oxides (IrO_2 and RuO_2) are the most studied OER electrocatalysts [4]. High cost and scarcity of these electrocatalysts limit their application for OER in industrial electrolysers [4]. On the other hand, low-cost copper and cobalt co-doped Ni_3S_2 supported on nickel foam (CuCo-Ni_3S_2/NF) electrocatalysts were examined for OER in 1 M KOH showing high catalytic activity and low OER overpotential [5]. Different types of zeolites could be an excellent choice for low-cost OER catalyst support because of the unique structure and large surface area [6]. The basic type of zeolite consists of two types of anionic groups: tetrahedral $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$ units charge-balanced with different positive ions such as sodium (Na^{1+}), silver (Ag^{1+}), nickel (Ni^{2+}), copper (Cu^{2+}) ions, etc. Different types of microzeolites (A and X) with Ni ions, studied in our previous work, showed OER catalytic activity and relatively good stability [6].

Herein, copper and nickel nanozeolites (CuX and NiX) were, for the first time, tested for OER in highly alkaline media by linear sweep voltammetry (LSW).

Polarization curves of CuX and NiX nanozeolites revealed that both of zeolite electrodes showed activity for ORR in alkaline media (1 M KOH). The current density of 1 mV s^{-1} was reached at overpotential of 530 and 670 mV for CuX and NiX zeolites, respectively. OER Tafel slopes at CuX and NiX electrodes were found to be 173 and 187 mV dec^{-1}, respectively. Significantly higher Tafel slope (463 mV dec^{-1}) was obtained for NiA zeolite in 1 M KOH [6]. A similar value of Tafel slope (144 mV dec^{-1}) was obtained at the Pt-modified Ni foam electrode in 1 M NaOH [3]. Co-Ni_3S_2/NF (150.9 mV dec^{-1}) and Cu-Ni_3S_2/NF (176 mV dec_{-1}) electrodes showed similar Tafel slope as herein tested electrodes [5]. CuX and NiX gave a current density of 8.5 and 1.20 mA cm^{-2} at 2 V vs RHE, respectively. CuX electrocatalysts gave lower overpotential, lower Tafel slope and higher OER current density than NiX which indicating its better catalytic activity during OER. Thus, low-cost CuX nanozeolite could be an excellent replacement for the expensive OER electrocatalysts based on scarce Pt-group metals or their oxides.

Acknowledgment

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Fluoride-ion Conduction Mechanism of La-Sr-F-S Mixed-anion Compounds

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Fluoride-ion batteries (FIBs) are expected to be one of the candidates for next-generation rechargeable batteries due to their high theoretical energy density. FIBs contain monovalent fluoride ion as ion carrier, which can realize the multi-electron reactions of counter cations utilizing fluorination/defluorination in active materials such as metal fluoride compounds or metals. This feature enables the high theoretical energy density of FIBs for approximately 5000 Wh L^{-1}[1]. It was demonstrated that all-solid-state FIBs using MFn (M = Bi, Cu, Sn, KBi) cathode and Ce anode with $La_{1-x}Ba_xF_{3-x}$ solid electrolyte performed charge/discharge cycles at 150°C in 2011[2]. The charge/discharge of liquid-type FIBs using Bi/BiF_3 cathode and Pb/PbF_2 anode with ionic liquid electrolyte at room temperature has been also reported in 2017[3]. Although all-solid-state batteries are expected to be used widely owing to their high energy densities, long life cycles, and safety, FIBs using solid electrolytes is far from practical use due to lack of solid electrolytes which have high ionic conductivity and wide electrochemical potential window like lithium-ion solid electrolytes.

The reported solid electrolytes such as $PbSnF_4$ [4] and $La_{0.9}Ba_{0.1}F_{2.9}$ [5] are well known fluoride ion conductors. $PbSnF_4$ exhibits the highest ionic conductivity of 2 mS cm^{-1}, whereas the electrochemical potential window is 0-2 V vs. SnF_2/Sn, which is disadvantage for the high voltage battery operation. To obtain solid electrolytes which have both high ionic conductivity and wide electrochemical potential window, it is necessary to use rather rare-earth metals than cations with their poor chemical stability in the low voltage such as Pb and Sn. $La_{0.9}Ba_{0.1}F_{2.9}$ also exhibits high ionic conductivity of 10^{-1} mS cm^{-1} having wide electrochemical potential window. Room temperature operation using the La-Ba-F electrolytes requires higher ionic conductivity than the present conductivity. Mixed-anion compounds have recently attracted attention, and unique structures with multiple anions have been reported [6]. Compared with existing materials such as oxides and fluorides, mixed-anion compounds have the possibilities to exhibit innovative functions due to their specific crystal and coordination structure.

In this study, we synthesized La-Sr-F-S compounds containing fluoride and sulfides ions as anions by solid-state reaction under vacuum. The crystal structure of the synthesized compound was characterized by X-ray diffraction. In order to measure the conductivity and the fluoride-ion transport number of the synthesized compounds, electrochemical impedance spectroscopy and the DC conductivity measurement were performed, respectively. Moreover, cyclic voltammetry was performed to evaluate electrochemical potential window. In the synthesis, F^-- deficient and F^--excess type of La-Sr-F-S compounds were successfully synthesized by controlling the weight ratio of starting materials. We discuss the mechanism to realize fast fluoride ion conduction comparing them.

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Visualization and Quantification of Electrochemical H_2 Bubble Nucleation at Pt, Au, and MoS_2 Substrates

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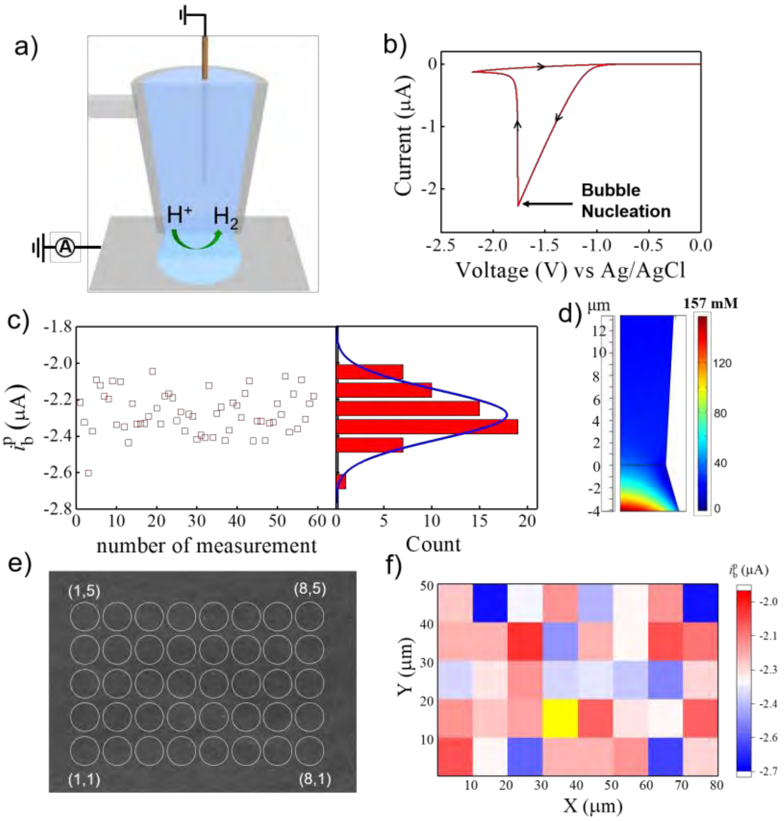
Electrolytic gas evolution is a significant phenomenon in many electrochemical technologies from water splitting, chloralkali process to fuel cells. Although it is known that gas evolution may substantially affect the ohmic resistance and mass transfer, studies focusing on the electrochemistry of individual bubbles are critical but also challenging. Here, we report an approach using scanning electrochemical cell microscopy (SECCM) with a single channel pipet to quantitatively study individual gas bubble nucleation on different electrode substrates, including conventional polycrystalline Pt and Au films, as well as the most interesting two-dimensional semiconductor MoS_2. Due to the confinement effect of the pipet, well-defined peak-shaped voltammetric features associated with single bubble nucleation and growth are consistently observed. From stochastic bubble nucleation measurement and finite element simulation, the surface H2 concentration corresponding to bubble nucleation is estimated to be ~218, 137, and 157 mM, with critical nuclei contact angles of ~156°, ~161°, and ~160° at polycrystalline Pt, Au, and MoS_2 substrates, respectively. We further demonstrated the surface faceting at polycrystalline Pt is not specifically correlated with the bubble nucleation behavior.



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Potential Range Extension for Electropolymerized Polypyrrole Films

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Polypyrrole (pPy) polymer materials attract much attention of researchers due to their original properties. Proposed methods for deposition of pPy coatings as well as for the synthesis of various pPy-containing composite materials has opened prospects for their use in a wide range of practical applications, such as molecular electronics, electrochemical sensors, supercapacitors, etc. [1-3]. One of the main methods of polypyrrole synthesis is the electrochemical method, the essence of which consists of electro-oxidation of the dissolved monomer on the electrode surface with the formation of a polymer film.

The overwhelming majority of papers on electrodeposited polypyrrole conclude that the resulting conjugated polymer possesses an electrochemical activity potential region of about 1 volt. Beyond the negative limit, this material turns to a neutral/insulating state. In contrast, at more positive potentials, the "overoxidation" process occurs, leading to irreversible degradation. Such a narrow electroactivity range is a disadvantage of this material, limiting its applicability, for example, as an active element of supercapacitors or as a matrix for electrodeposition of most metals in the synthesis of composite metal-polymer catalysts/sensors. However, it was mentioned [4] that low deposition potentials and low monomer concentrations allows to obtain the polypyrrole films exhibiting electroactivity in the broader range of potentials. This change is irreversible and can occur either immediately after synthesis (electropolymerization) or during repeated cycling of the film in an extended potential limits.

The goal of this work is to study and to optimize the method of electrodeposition of polypyrrole under non-conventional conditions (ensuring a low rate of polymer formation on the electrode surface), as well as to investigate the structure and properties of the obtained promising materials. For that propose, we have studied several factors (concentration of pyrrole during electrodeposition within a sub-mmol range, oxidation potential, the thickness of the polymer coating, multi-scan parameters of the obtained polymer film, and the composition of electrolyte solution) affecting the electroactivity range of polypyrrole. Thus, the conditions for subsequent purposeful enhancement of this effect have been figured out.

Acknowledgments

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Anodic generation of EDOT cation radicals for PEDOT-PSS Dispersion Synthesis

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Conducting organic materials and coatings based on poly 3,4-ethylene dioxythiophene (PEDOT) are currently a principal component of electrochromic coatings, displays, capacitors, photoelectric converters, and several other devices. The range of PEDOT applications is expanding due to intensive scientific research in this area. In most applications, PEDOT is used as part of a composition with polystyrenesulfonate anion (PSS) [1, 2]. Usually, the precursor for its preparation is an aqueous dispersion of PEDOT-PSS (fig. 1) representing a commercially available product. Its synthesis based on the chemical oxidation of a mixture of peroxodisulfate precursors anion, followed by ion-exchange purification from the products of the oxidant reduction and auxiliary substances [3]. The studies in this work are aimed at developing the fundamental principles and practical implementation of the electrochemical method for preparing a dispersion of PEDOT-PSS, consisting in the generation of EDOT radical cations on the surface of a porous anode with continuous intensive pumping through it of a polymerization medium containing a PSS polyanion without using an oxidizing agent.

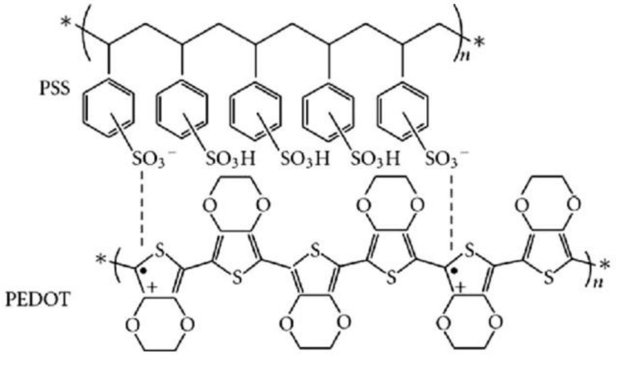

Fig. 1. Chemical structure of PEDOT:PSS

Electrooxidation of EDOT was carried out in a solution of polystyrenesulfonic acid (HPSS) at the working electrode with simultaneous pumping of the polymerization medium through the pores of the electrode at a given speed. PEDOT-PSS dispersion was synthesized in a special electrochemical cell with separated electrode spaces, through the anode of which an intensive pumping of the polymerization medium containing the monomer and polyanion is carried out. In addition to the direct oxidation of EDOT in the presence of HPSS, a redox mediator oxidation of EDOT in the presence of HPSS and a redox mediator was performed. The resulting suspensions were characterized by a complex of electrochemical, microscopic, and spectral methods.

Acknowledgments
The study was supported by RFBR (project № 20-03-00966 A) and carried out within the framework of the thematic map of the IPCP RAS №AAAA- A19-119061890019-5 with the use of resources of National Technology Initiative Competence Center at IPCP RAS.

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Enhanced Performance of Spinel $LiMn_{1.5}Ni_{0.5}O_4$ Controlled by Oxygen Vacancy

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The spinel $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) is a promising cathode material for lithium-ion battery because of its high working voltage: 4.7 V, considerable cost, high capacity and energy [1-3]. However, its structural relationship with the electrochemical properties is still a challenge [5, 6]. The electrochemical properties of the spinel are related to the degree of disorder, doping, impurities, Mn^{3+} content, morphology and oxygen vacancy, among others. Oxygen vacancy is identified as a key structural factor because of its correlation with the degree of disorder and Mn^{3+} content [5]. In this research works, we examined the relationship among the structural parameters (oxygen vacancy, disordered phase, Mn^{3+} and impurity contents); and their electrochemical effects. This work revealed for the first time the use of oxygen vacancy: β-MnO_{2-x} as precursors to synthesised spinel LMNO cathode materials and tune the oxygen vacancy, disordered phase, Mn^{3+} content and impurity contents without doping, higher synthetic temperatures (› 700 °C), use of organic compound, post-annealing or modification of the cooling profile. We showed that varying synthetic conditions of β-MnO_{2-x} can tune these structural factors in LMNO for improved electrochemical performance. The results of the studies showed that the oxygen vacancy changes concurrently with the degree of disorder and Mn^{3+} content, but not with the impurities. Our study has opened opportunities to explore the use of β-MnO_{2-x} to tune these structural factors in spinel LMNO for an improved lithium-ion battery.

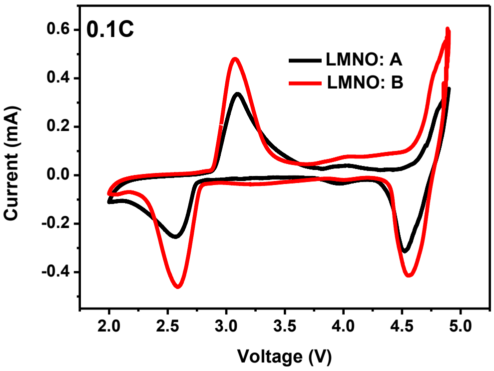

Fig 1. Cyclic voltammogram

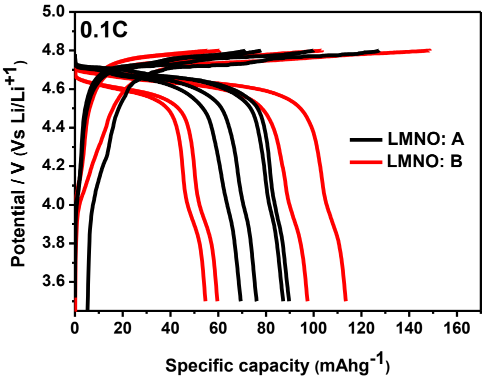

Fig. 2 Charge-discharge: 1st, 2nd, 25th and 50th cycle

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Fuel Cell Production Techniques for Self Reliance and Sustainable Development in Nigeria.

By

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Abstract

Fuel cells are electrochemical devices that convert chemical energy in fuels into electrical energy directly with promising power generation, high efficiency and low environmental impact. Fuel cell production techniques avoids the intermediate steps of producing heat and mechanical work common with most conventional power generation and are not limited by thermodynamic limitations of heat engines such as the Carnot efficiency and produce power with minimal pollutant since combustion is not involve in the production and operation techniques. This paper examines fuel cell production techniques as a clean sources of renewable energy, types of fuel cell, advantages and disadvantages of various fuel cells were also investigated. It also compares the cost effectiveness of small scale fuel cell power plants with that of large scale vis a vis other renewable source. The paper concluded that fuel cell is an essential component of sustainable energy mix for self reliance of power sector in Nigeria.

Key words: Carnot efficiency, electrolyzers, unit cells, phase interface and fuel cell stacking.

Room-Temperature Conversion of the Photoelectrochemical Oxidation of Methane into Electricity at Nanostructured TiO_2

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The energy potential of methane is restrained by the energy input required to break its C-H bond. Therefore, most of the energy conversion processes of methane use thermochemical activation which is highly endothermic. The present work demonstrates the effective photoelectrochemical (PEC) activity of a TiO_2 nanotube arrays photoanode towards methane oxidation in acidic electrolyte and ambient conditions. PEC processes can dramatically reduce the activation barrier by the interaction with light. The use of a semiconductor photoanode in a PEC system can produce highly reactive holes upon irradiation, aiming for the activation of methane's C-H bond at moderate temperatures. The examined photoanode exhibits high photocurrent density response in the presence of methane as compared to that obtained in its absence (0.54 vs. 0.27 mA cm^{-2}, respectively). Products characterization reveals a relatively high faradaic efficiency towards the formation of CO_2 and formic acid (72 and 16% at 0.3 V vs. RHE, respectively). These results are correlated to the role of the special surface architecture of the nanotube arrays in dictating the reaction pathways. The first time room-temperature operation of a solar driven fuel cell (photo-fuel cell), in which methane oxidation is converted to electricity, is also demonstrated. The photo-fuel cell performance is characterized by a relatively high power density (69 µW cm^{-2}), when compared to such cells with liquid fuels, as well by long-term stability.

Lithium-Ion High-Performance Anodes using Silicon Nanowires/Graphite Composites

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Lithium-ion batteries (LIBs) have enabled significant technological progress in recent years and are considered the state-of-the-art technology for electrochemical energy storage [1]. Yet, these LIBs still require substantial improvements in their power and energy density, particularly for applications in electric vehicles [2]. Most commercial LIBs use graphite, an intercalation-type material with excellent cycling stability, as negative electrode. However, its rather low theoretical capacity of 372 mAh g^{-1} and slow Li-ion intercalation kinetics result in an overall low volumetric energy density and poor rate performance.

The use of silicon nanowires/graphite composites is of particular interest, because it is anticipated to allow for combining the advantages of the two components – i.e., the excellent cycling stability of the carbon-type material and the much greater specific capacity (3579 mAh g^{-1}) and good rate capability of silicon. Indeed, the much greater specific capacity potentially allows for an increased volumetric and gravimetric energy density when combined with a suitable cathode in LIBs [3]. Furthermore, silicon is non-toxic and abundant in the earth's crust, rendering it a good candidate for high-performance and sustainable negative electrodes. The 1D silicon nanowire morphology compared to bulk silicon materials offers short Li^+ transport pathways [4] and provides better contact with the graphite particles within the composite.

Herein, we report on the evaluation of silicon nanowires/graphite composites (engineered wires composites) as lithium-ion anode active material. The structural and morphological investigations were carried out using amongst others x-ray diffraction, transmission electron microscopy, and scanning electron microscopy. Furthermore, we present our comprehensive electrochemical investigation of this material with galvanostatic dis-/charge tests in lithium-ion half-cells and full-cells using Ni-rich NMC as the cathode. The results reveal very good cycling stability and rate performance – even for high areal capacities in coin cells and in pouch cells.

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N-doped Mesoporous Carbon Spheres from m-Aminophenol and Pluronic® F127 Template as Support for ORR Catalysts

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Despite the large and growing interest of polymer electrolyte membrane fuel cell (PEMFC) as an energy converter, high cost, relatively insufficient activity and long-term stability of the catalyst materials remain major obstacles for commercialization. Platinum is still considered as the state-of-art for catalyst material in PEMFC. However, it exhibits a slow kinetics for oxygen reduction reaction (ORR) that is mostly due to the strong bond of the oxygen molecules. The long-term efficiency of the electrodes is strongly influenced by the nature of the catalyst support that should allow optimal distribution and stabilization of the catalyst nanoparticles [1]. Most common mesoporous carbon syntheses rely on hard-template, time-consuming routes that are not suitable for industrial scale-up. Therefore soft-template methods appear to be more adapted.

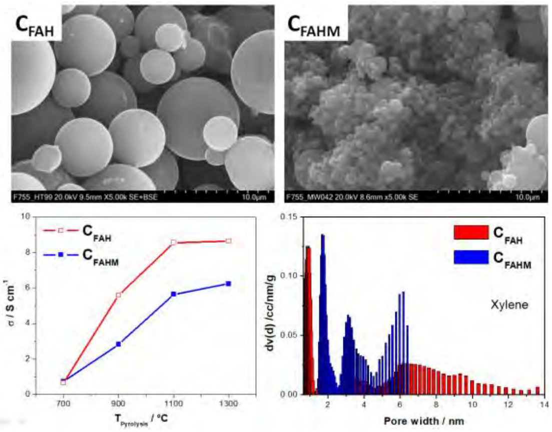

Fig.1: SEM image, conductivity and pore size distribution profile of as-prepared carbon

In this work, synthesis of carbon powder samples was prepared by autoclave hydrothermal (C_{FAH}) and microwave-assisted hydrothermal (C_{FAHM}) route by using *m*-Aminophenol as carbon source and triblock-copolymers Pluronic F127 as soft-template. Characterization of the as-prepared carbons was performed by means of XRD, Raman, TGA, BET and SEM. All synthesis led to formation of spherical carbon particles (Fig. 1) with diameter between 5.0 µm (C_{FAH}) and 0.7 µm (C_{FAHM}). By varying heating time, power of heat source, reaction temperature, reaction time of microwave reactor during polymer synthesis as well as optimizing pyrolysis temperature (T_{py}), the size of carbon particle was successfully reduced from 3.0 down to 0.7 µm. Reaction time for polymer synthesis was substantially reduced from 12 h for common hydrothermal route down to 5 min for microwave-assisted one. The pore size of carbon particles was successfully tuned from micro- to mesoporous (5 – 15 nm) range by using xylene, toluene or ammonium bicarbonate as a pore forming agent. The electronic conductivity of carbon particles was enhanced from 0.6 to 5.6 Scm^{-1} at 100 Ncm^{-2} by increasing pyrolysis temperature from 700 to 1100°C (Fig.1). The N content of carbon was found within 8 – 10 wt% at 900°C (T_{py}). Then, carbon particles were decorated with 40 wt% Pt by chemical impregnation/reduction of hexachloro-platinic acid in formaldehyde at 80°C for 1 h. Electrochemical activity of Pt/C catalysts for ORR was studied under RRDE and GDE conditions. The highest performance regarding ECSA retention during accelerated degradation tests (0.4-1.4 V, dE/dt = 1 V s^{-1}, 10,000 cycles) was achieved by Pt/C_{FAH} with 77% followed by Pt/C_{FAHM} with 75%, compared to only 8% for Pt/C_{Vulcan}. Best performance in terms of synthesis duration, particle size, conductivity, pore size distribution, Pt activity for ORR and ECSA retention was achieved by carbon powder from microwave-assisted hydrothermal synthesis route.

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Electrochromic response of WO_3 layers grown using magnetron sputtering under various pressures

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Last decades, scientific interest has been attracted for electrochromic coatings, since these are essential in a variety of novel technological applications such as switches, batteries and smart windows. Tungsten trioxide is one of the most common electrochromic film for smart window applications that can be used in order to reduce the energy consumption on buildings. To date many methods, such as sol-gel, hydrothermal synthesis, chemical vapour deposition (CVD) and magnetron sputtering, have been used for the deposition of WO3 layers. As has been shown, one very important parameter for the response of the layers is their morphology.

In this work, amorphous WO3 coatings were grown on indium tin dioxide glass substrates using magnetron sputtering with tungsten target and various amount of vacuum in the deposition chamber. The coatings were characterized by X-ray diffraction, XPS, UV-Vis-IR spectroscopy, scanning electron microscopy and cyclic voltammetry in order to investigate the importance of their porosity in the improvement of their electrochromic performance, including durability, time response, charge density and coloration efficiency.

Acknowledgements:
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Electrodeposition of Ni and Composite Ni/TiO_2 Coatings Using an Electrolyte Based on Deep Eutectic Solvents with Water Addition

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Electrochemical deposition of nickel and nickel-based coatings is considered as the most significant and widespread metal finishing in up-to-date industry. Ni and Ni-based coatings can be deposited from "common" aqueous electrolytes, however these have a lot of drawbacks. Recently, some attempts were made to use a new type of electrolytes based on the so-called deep eutectic solvents (DESs) [1, 2]. DESs are ionic liquid analogues, which consist of eutectic mixtures of some inorganic and/or organic compounds. DESs show a number of excellent and useful properties, such as wide electrochemical potential window, high conductivity, negligible vapor pressure, easy accessibility, environmental safety and biodegradability [1]. Therefore, DESs attract close attention in electrochemistry, especially in electroplating [1, 2].

We investigated the electrodeposition of nanocrystalline nickel and composite Ni/TiO_2 coatings using a plating bath based on a deep eutectic solvent which is commercially known as ethaline (a eutectic mixture of ethylene glycol and choline chloride) [3–7]. Titania nanopowder (Degussa P 25, 25–30 nm) was used to prepare colloid electrolytes for electrodeposition of composite coatings.

It was established that the addition of some water to the nickel plating bath provides a decrease in viscosity and an increase in conductivity [3, 4]. An irreversible electrochemical reaction of metal deposition is decelerated when water is added to the ethaline + $NiCl_2$ solutions.

The electrodeposited nickel coatings exhibit an average crystallite size of about 3–9 nm. According to electrochemical impedance spectroscopy measurements, the coatings with enhanced corrosion resistance can be obtained from Ni electroplating bath containing some water additive.

Due to relatively high viscosity and density, DESs ensure excellent dispersion stability as compared with "common" aqueous solutions. The content of TiO_2 in deposits reaches 10 wt.%. The composite Ni/TiO_2 coatings show nano-sized type of structure.

The formation of composite coatings based on the nickel matrix provides an appreciable improvement in functional properties of deposits. Thus, their microhardness is higher and the corrosion resistance in a corrosive medium is better than in the case of pure Ni coatings. The incorporation of TiO_2 particles imparts the photocatalytic activity towards the photochemical degradation of organic dyes and the electrocatalytic activity in the hydrogen and oxygen evolution reactions to the synthesized composite coatings.

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Synthesis of Polymer-TiO_2 Nanofiber Membranes and Their Photocatalysis Properties

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ABSTRACT

Polymer/semiconductor oxide composite fibers prepared by electrospinning is a multifunctional material. The components can be joined by covalent bonds, electrostatic attraction or other weak interaction forces, possessing combined properties of inorganic component and high molecular polymer. The addition of polymer can stabilize transition metal oxide and avoid agglomeration of nanoparticles during the photocatalytic process. At the same time, transition metal oxide can increase the surface area and porosity of fiber, giving full play to the adsorption and photocatalytic performance.

In this project, electrospinning method has been used to synthesize semiconductor metal oxide nanocomposites. Polyacrylonitrile (PAN) is the polymer matrixes to hold titanium dioxide (TiO_2) nanoparticles. Polyvinyl Pyrrolidone (PVP) is added as a pore-forming agent. Porous and flexible nanofiber membrane with high TiO_2 content was prepared by selectively dissolving PVP. SEM, BET, CA, XRD, FTIR, TGA and DSC were used to characterize the surface morphology, microstructure, composition and thermal stability of the fiber membrane. The effects of different pore-forming agents on the coupling adsorption and photocatalytic reaction of fiber membranes were investigated.

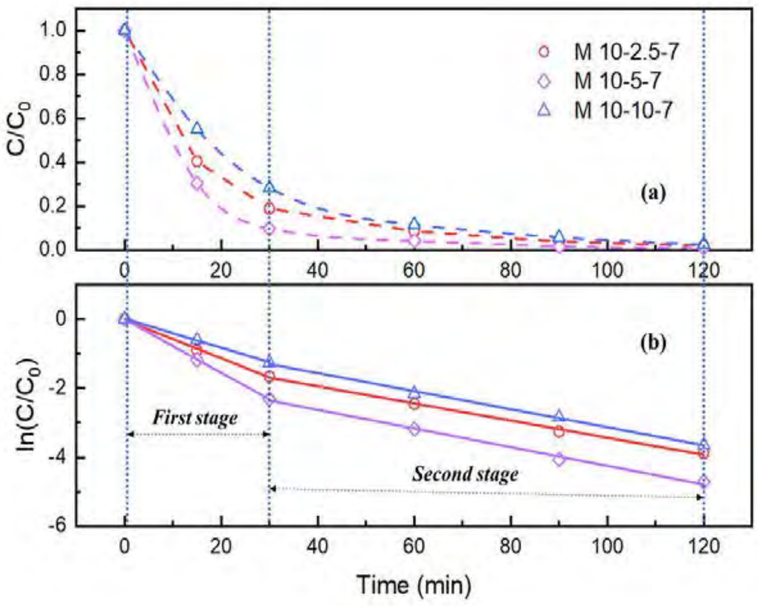

Figure 1 Adsorption and photocatalytic processes of methylene blue: (a) Degradation rates, and (b) fitting the pseudo-first-order kinetics. 300 w simulation sunlight.

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Electrochemical Detection of DNA using Methylene Blue as a Marker

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The detection of genetic diseases at early stage in clinical diagnosis requires the development of reliable, highly sensitive and selective genosensors capable of detecting single-nucleotide polymorphisms (SNPs)[1]. In contrast to traditional methods such as colorimetric, plasmonic, electrochemical sensors have advantages such as simplicity, low cost, ease of miniaturization, rapid response times and high sensitivity, required for this application.

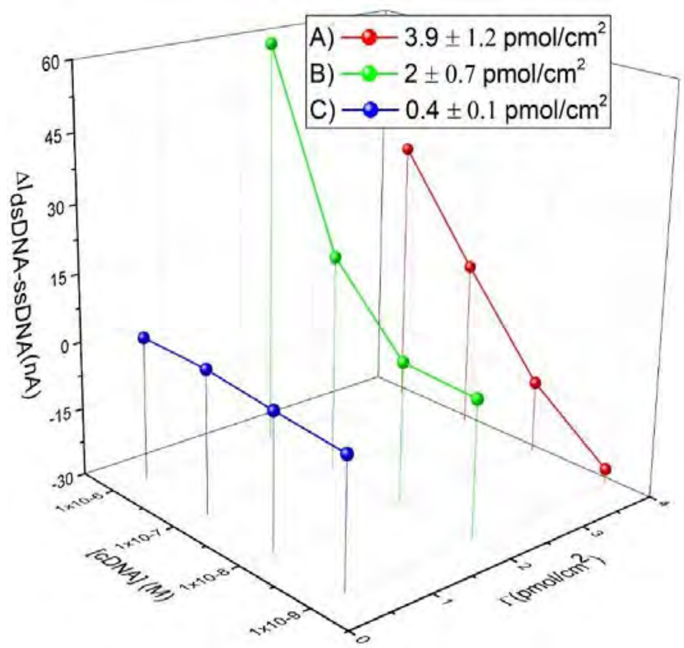

Figure.1 Influence of the probe surface coverage and concentration of cDNA on the signal increase upon hybridization. Results obtained via DPV in PBS at pH 7.4

The majority of electrochemical methods of detection of DNA are based on hybridization processes. These approaches offer high selectivity for the target DNA and low limits of detection, (LOD) approaching zeptomolar levels, that can enable the detection of disease at early stages. Nevertheless, the detection of SNP genosensors are still not available and such sensors would fill a significant need[2]. The detection of the TP53 cancer biomarker has been investigated electrochemically by monitoring changes in DNA structures before and after hybridization p with a maximum signal gain upon hybridization of 59.6 nA at a surface coverage of 2.0 pmol/cm^2 (Figure.1). The selectivity of the DNA biosensor was investigated using three types of tDNA sequences: complementary DNA, single base mismatch and triple base mismatch. The biosensor is capable of discriminating between a normal healthy sequence and a triple base mismatch with a discrimination factor of 8. The electrochemical signal gain upon hybridization with single base mismatched sequence is similar to that observed with cDNA, indicating that the biosensor is not capable of discriminating between normal and and single base mismatches.

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Irreversible Reaction of $LiFePO_4$ - $Li_4Ti_5O_{12}$ Full-cell Using Two-phase Reaction Active Material

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For charge-discharge test in laboratory experiments of lithium-ion batteries, half-cell configuration with lithium as the anode is often used. In contrast, for practical lithium-ion batteries, lithium metal is not used for the anode, but full-cell configuration is used, in which the capacity of the anode is almost similar to the capacity of the cathode. While the half-cell configuration has lithium as a source of excess carrier ions in the anode, in the full-cell configuration, only the limited lithium-ions supplied from the cathode are used as carrier ions, limiting the actual charge-discharge capacity of the full-cell. Previous studies have reported differences in the degradation behavior between full-cell and half-cell [1,2]. It is important to understand the unique problems that occur with full-cell in order to maximize the performance of lithium-ion batteries in practice. In this research, we investigated the irreversibility in full-cell with lithium iron phosphate ($LiFePO_4$) cathode and lithium titanate ($Li_4Ti_5O_{12}$) anode as a strange case, where both active materials show two-phase reaction in almost all composition. In addition to the electrochemical measurements used three-electrode cell, the X-ray absorption fine structure (XAFS), which allows to observe the valence change, was used to determine the charge-discharge state in the full-cell.

In a constant-current charge-discharge measurement at 0.1 C in a half-cell, the charge-discharge reaction proceeded reversibly with a capacity of 155 mA h g^{-1} in the $LiFePO_4$ cathode and 150 mA h g^{-1} in the $Li_4Ti_5O_{12}$ anode. However, in our experiments, we observed an irreversible reaction in the $LiFePO_4$ - $Li_4Ti_5O_{12}$ full-cell configuration, with a capacity decrease with each cycle. The initial charge and discharge capacity were 162 and 126 mAh g^{-1}, respectively and this irreversibility was continuously observed in the subsequent cycle (Fig. 1). By using the three-electrode cell, we analyzed the potential changes of the cathode and anode. The potential of the anode increased and reached the cut-off voltage during the discharge before the change of the cathode. The valence states of the cathode and anode expected to be similar composition during charging and discharging (Li_xFePO_4 x = 1.00, 0.30 0.07) were examined by XAFS. Fe K-edge XAFS shown similar edge energy for the charged and discharged $Li_{0.3}FePO_4$ cathode. However, Ti K-edge XAFS of charged $Li_{5.8}Ti_5O_{12}$ anode shown the different edge energy from that of the discharged anode, which agrees with the results from the three-electrode test. Therefore, the irreversible capacity was caused by the shifting of state of charge in anode due to some side reactions on the $Li_4Ti_5O_{12}$ anode side during charge reaction.

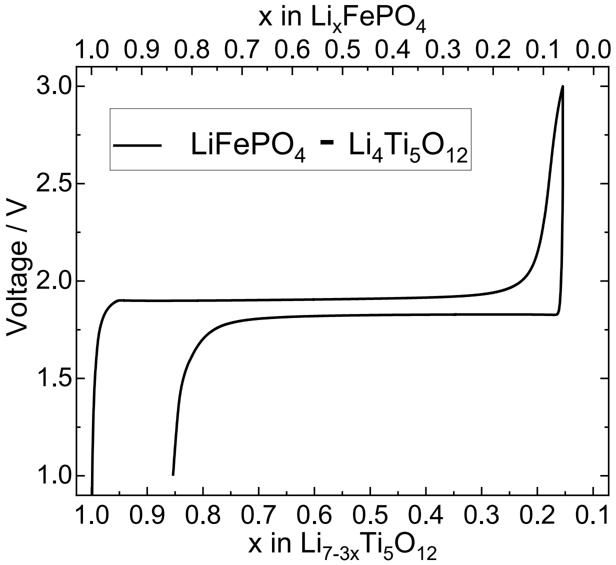

Fig.1 $LiFePO_4$ - $Li_4Ti_5O_{12}$ full-cell charge-discharge profile at 0.1 C.

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Surface Characterization of Indium Tin Oxide to Investigate the Effect of Modification on its Response to Molecules

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Abstract

The relationship between surface properties of indium tin oxide (ITO) and its effect on surface modification and response to several biomolecules was investigated. ITO substrates were selected to compare the effect of its electrochemical surface properties on the voltammetric measurement. It was found that a small difference in surface properties affect the rest potential of ITO electrode in the electrolyte. In addition, surface properties can effectively change the monolayer modification properties and it was revealed that optimization of surface properties is important to get selective response for biosensor development.

$AuCeO_2/C$ as electrocatalysts towards ethylene glycol oxidation and oxygen reduction reactions

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Different fuels such as methanol, ethanol, ethylene glycol or others recently have been used in direct alcohols fuel cells (DAFC). However, because of low methanol electro-oxidation kinetics and complication of getting the clean catalytic process using ethanol, ethylene glycol seems more reasonable as a fuel for DAFC due to its low toxicity, uncomplicated storage, easy transportation and production from biomass.

It is especially important to create and develop effective catalysts not only for fuel oxidation, but also for oxygen reduction. In this case Au was considered as one of the best catalysts for the fuel cell reactions in alkaline medium, due to its surface resistance of poisoning for the intermediates, which allows to achieve high electrocatalytic activity towards alcohols oxidation and oxygen reduction reactions. It is known that addition of metal oxides, such as CeO_2, Co_3O_4, SnO_x, MnO_2 or RuO_2 enhanced the electrocatalytic activity towards oxidation of ethylene glycol and reduction of oxygen. Cerium oxide is attractive because of its low price, synergistic effect between CeO_2 and gold and tolerance to the CO poisoning.

In this paper was investigated the electrocatalytic activity of $AuCeO_2/C$ and Au/C catalysts prepared by the adsorption of AuNPs on the CeO_2/C and C substrates from an Au colloidal solution. The composition, morphology and structure of the prepared catalysts have been characterized using Inductively Coupled Plasma Optical Emission Spectroscopy, Field Emission Scanning Electron Microscopy, X-ray photoelectron spectroscopy and X-ray Diffraction. Electrocatalytic properties of the prepared $AuCeO_2/C$ and Au/C catalysts have been investigated towards the oxidation of ethylene glycol in an alkaline medium using cyclic voltammetry, whereas the reduction of oxygen has been investigated by means of the linear sweep voltammetry using the rotating disk electrode method.

It has been found that the $AuCeO_2/C$ catalyst showed ca. 3 times higher electrocatalytic activity towards the oxidation of ethylene glycol compared to that of Au/C. Moreover, $AuCeO_2/C$ showed more positive onset potential, as well as higher current density in the mixed-kinetic-diffusion region towards ORR in an alkaline medium compared to that at the bare Au/C catalyst.

Selective Electrochemical Xanthine Biosensor based on PEDOT: PSS and Functionalized Gold Nanoparticles Nanocomposite Platform

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Abstract

An innovative biosensor assembly relying on glassy carbon electrode modified with nanocomposites consisting of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as a host matrix with functionalized gold nanoparticles (GCE/PEDOT:PSS-AuNPs) is presented for the selective and sensitive detection of xanthine (XA). The developed sensor was successfully applied for the quantification of XA in the presence of significant interferences like hypoxanthine (HXA) and uric acid (UA). Different spectroscopy and electron microscopy analyses were done to characterize the as-prepared nanocomposite. Calibration responses for the quantification of XA was linear from 5.0×10^{-8} to 1.0×10^{-5} M ($R^2 = 0.994$), with detection limit as low as 3.0×10^{-8} (S/N = 3). Finally, the proposed sensor was applied for the analyses of XA content in commercial fish and meat samples and satisfactory recovery percentage was obtained.

Keywords: Electrochemical biosensor; PEDOT:PSS, gold nanoparticle; nanocomposite; xanthine.

Atomistic insights into the structural, transport and electrochemical properties of biredox ionic liquids from molecular dynamics

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Biredox ionic liquids are a new class of functionalized electrolytes that are receiving increasing consideration for use in capacitive energy storage devices. They differ from conventional electrolytes in that both cations and anions are functionalized with redox-active moieties, [1] which may actively participate in the storage mechanism via electrochemical reactions at the electrode interface. In this work, TEMPO and anthraquinone are used as the redox active species. Given that these types of biredox systems are relatively new, much remains to be understood about the relationship between the size/volume of the IL cation/anion moiety, the solvent structure and dynamics, and the electrochemical properties of each system.

Here, we employ first-principles molecular dynamics to study biredox ionic liquids dissolved in acetonitrile. We investigate several combinations of anions and cations, differing in the hydrodynamic radius and we compare them with the bare redox molecules. We show that in all cases, it is necessary to introduce a two-Gaussian-state model to calculate the reaction free energies accurately, which are found to be slightly affected by the presence of the IL group on the molecule. MD simulations also provide the atomistic details used to characterize the structure of the solvation shell around the redox active part of the molecules. Our investigations suggests that for TEMPO-based molecules in particular, a strong effect of solvent reorientation influences the electron transfer process.[2] This study represents a first step in the understanding of electron transfer processes in these complex systems and will hopefully contribute to the design of new ionic liquids with better performances for use in energy storage devices.

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Electrochemical Synthesis of Organic/inorganic Hybrid Nanoantimicrobials (NAMs) Fighting Antimicrobial Resistance (AMR)

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Chitosan (CS), a natural non-toxic polysaccharide, shows intrinsic antimicrobial activity against a wide range of pathogens. CS and CS-based biomaterials can be effective additives in food and medicine-related industries to inhibit growth of pathogens. The application of inorganic nanophases, such as metal and metal oxide nanoparticles, has received attention due to their broad and pronounced antimicrobial activity. Upon combination with CS, which can act as stabilizer, with active inorganic nanophases, robust synergistic nanoantimicrobial (NAM) systems can be produced. These hybrid NAMs offer an alternative strategy to fight antimicrobial resistance and overcome limitations of conventional antibiotics. Bioactive ZnO, Cu and Ag nanophases produced by green electrochemical approach [1] can be combined with antimicrobial CS to develop synergistic antimicrobial nanohybrids with amplified biological action. CS-based NAMs were preliminary characterized by electron microscopies and spectroscopic techniques. Hybrid NAMs may find application in the control and inhibition of biofilm growth.

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Acknowledgements

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In Situ Activation of Anodized NiFe Alloys for OER in Alkaline Media

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Because of the limited availability of fossil fuels and global environmental issues, hydrogen production by electrochemical water splitting using renewable energy sources becomes of increasing importance for future hydrogen economy. Currently, hydrogen is mostly produced from oil, coal and natural gas, and the processes generate also greenhouse gases as byproducts. Although fuel cells using hydrogen as a fuel are commercially available, this technology is still using fossil fuels to produce hydrogen. Thus, clean hydrogen production technology using renewable energies, such as solar, wind, water-based and biomass-based ones needs to be developed.

The main issue to utilize electrochemical water splitting for clean hydrogen production is sluggish kinetics of oxygen evolution reaction (OER). The oxides of Ru and Ir are known to show high activity and durability for OER, but their limited natural resources and high cost hinder their wide application to energy conversion and storage. Currently, extensive efforts are directed towards the development of noble-metal-free electrocatalysts for OER. In the present study, simple anodizing of NiFe alloys is used to develop a highly active electrode for OER.

The NiFe alloys with a range of Fe contents up to 21 at% were prepared by electrodeposition on Ni substrate. Then, the NiFe alloy deposits were anodized at 10 V in ethylene glycol electrolyte containing 0.2 mol dm^{-3} NH_4F and 0.1 mol dm^{-3} H_2O to form nanoporous anodic films. The OER activities were examined in 1.0 mol dm^{-3} NH_4F by cyclic voltammetry at a potential sweep rate of 10 mV s^{-1}.

The Fe content in the NiFe deposits increased almost linearly with the Fe^{2+} concentration in the deposition bath. The porous anodic films of ~400 nm thickness were formed by anodizing of the NiFe deposits in the ethylene glycol electrolyte containing NH_4F and H_2O. The STEM/EDS analysis of the anodic film indicated that Ni, Fe, O and F were distributed uniformly in the anodic film. The anodic film contained a crystalline phase of NiF_2 and the EDS analysis discloses the high concentration of fluoride in the anodic film. The Fe to Ni ratio in the anodic film was similar to that in the alloy deposit.

The OER activity of the anodized NiFe increased largely with CV cycling in KOH electrolyte. Thus, in situ activation occurred during potential cycling and the activation was much more significant in the anodized NiFe compared with the anodized Ni. The OER activity was largely composition dependent; the highest activity was obtained for the Ni-11.8 at% Fe, which showed the onset potential of OER as low as 1.49 V vs RHE. During in situ activation, ECSA increased by 3-5 times, but the OER current increased more markedly. More active sites for OER appeared to be developed during the potential cycling in KOH electrolyte.

Bidimensional spectroelectrochemistry. A new approach to compare the electrochemical behavior of modified electrode surfaces.

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Bidimensional spectroelectrochemistry (Bidim-SEC)[1,2] is an analytical technique that allows recording in a single experiment information related to the electron transfer process occurring at the working electrode (WE) surface from three very different points of view. The first one comes from the electrochemical signal that includes all the aspects directly related to the oxidation or reduction process provoked by the potential or current applied to the electrochemical system. The other two arise from simultaneously recording the spectral changes taking place during the electron transfer process. Specifically, the electromagnetic radiation samples the solution adjacent to the WE in a normal (perpendicular) and parallel direction respect to it, deconvolving the information related to the processes mainly occurring at the WE surface and those taking place exclusively on the diffusion layer.

In this work, a new cell (Fig. 1) is developed that allows two Bidim-SEC experiments to be performed at the same time. In this way, it is possible to compare in the same experiment, for example, the consequences or effects that the modification of the electrode surface has with respect to the process of oxidation or reduction of a certain molecule. The new Bidim-SEC cell is tested modifying partially a HOPG surface with a thin film of SWCNTs and comparing the electrochemical and spectroscopic response of different molecules such as ferrocenomethanol (takes as test molecule), dopamine or 3,4-ethylenedioxythiophene.

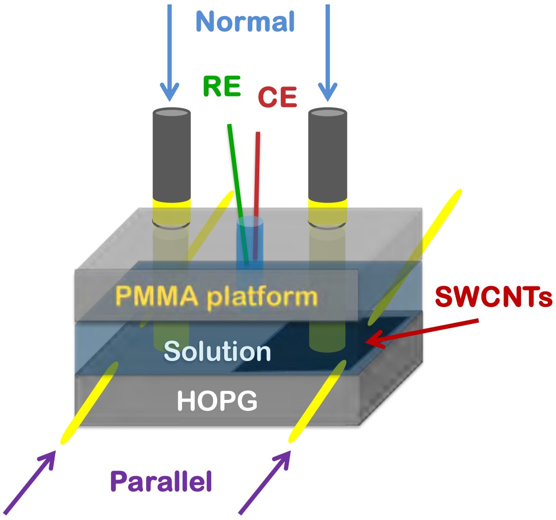

Fig. 1. Scheme of the Bidim-SEC platform

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Evaluation of Silver-Polyaniline-Polyvinylpyrrolidone Samples for The Borohydride Oxidation Reaction

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In recent decades, direct borohydride fuel cell (DBFC) has attracted great attention because of its high theoretical power density (9 kWh kg^{-1}), high theoretical open circuit potential (1.64 V) with environmental benign reaction products [1–3]. Borohydride oxidation reaction (BOR) occurs at the anode side (**Eq. 1**) while oxygen reduction reaction (ORR) occurs at the cathodic side (**Eq. 2**) in a DBFC. Thus, the overall reaction of DBFC is given by **Eq. 3.**

Oxidation: $BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-$ ($E^0 = -1.24$ V vs. SHE) (1)
Reduction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ($E^0 = 0.40$ V vs. SHE) (2)
Overall reaction: $NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O$ ($E^0_{cell} = 1.64$ V) (3)

The electrochemical oxidation of BH_4^- ion at the anode side is a very complex process where anode catalyst plays the main role. The borohydride hydrolysis reaction (BHR) has a competitive role with BOR leading to the generation of hydrogen bubbles and at the same time to decrease of the performance of DBFC [1]. The direct borohydride reaction could be presented by **Eq. 4** where n is the actual number of exchanged electrons. Literature reports suggested that only gold (Au) and silver (Ag) could exchange $8e^-$ during electrochemical oxidation of each BH_4^- ion [1,4].

$BH_4^- + nOH^- \rightarrow BO_2^- + (n-2)H_2O + (4-0.5n)H_2 + ne^-$ (4)

B. Molina Cocha and M. Chatenet [5] showed that the BOR mechanism on Ag catalyst depends on electrolyte solution pH where increasing pH value leads to an increase in the number of exchanged electrons. In our previous work [4] was shown that Ag incorporated into three different types of zeolites offered low onset potential and high BOR current densities.

Herein, we tested three silver nanoparticles (AgNPs)-polyaniline(PANI)-polyvinylpyrrolidone(PVP) with different amount, morphology and size of AgNPs electrocatalysts for BOR at pH 14 by cyclic voltammetry (CV). Ag-PANI-PVP electrocatalysts with 3.4, 43.8 and 18.9 wt% of Ag were noted as Ag-PANI-PVP-1, Ag-PANI-PVP-2 and Ag-PANI-PVP-3 respectively

All three Ag-PANI-PVP electrocatalysts showed good BOR activity in the potential range from -0.6 to 0.3 V vs SCE with appearance of several oxidation peaks. In this potential range, AgOH layer and Ag oxides are formed on the surface of Ag-PANI-PVP electrocatalysts in 2 M NaOH [6] which indicated that this Ag forms catalysed BOR. CVs of Ag-PANI-PVP-2 and Ag-PANI-PVP-3 electrocatalysts showed well defined and high intensity oxidation peak a_1 while CV of Ag-PANI-PVP-1 showed a broad peak of significantly lower intensity. Namely, a_1 peak current densities of 1.29, 1.27 and 0.14 mA cm^{-2} were recorded at Ag-PANI-PVP-2, Ag-PANI-PVP-3 and Ag-PANI-PVP-1 respectively. a_2 oxidation peak was observed only in case of Ag-PANI-PVP-1 electrocatalyst. BOR mechanism continues to be a subject of discussion, but peaks a_1 and a_2 could appear~~ed~~ due to the oxidation of hydroxyborohydride ion (BH_3OH^-) produced by the hydrolysis of $NaBH_4$ and BOR, respectively [4]. Ag/C and bimetallic Cu-Ag/C electrocatalyst showed anodic peaks during BOR at the same position [7].These electrocatalysts offer a great opportunity for improvement of performances of DBFC, because of their low-cost, easy synthesis and good electrochemical behaviour during BOR.

Acknowledgement

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Electron Transfer Between The Photoactive Protein And Redox Polymer Occurs Within Microsecond Time Scale

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Recently, there is more and more research on the biohybrid photoelectrochemical systems being conducted. While the photoactive proteins usually maintain charge separation quantum yields close to 100 % the further steps of electron and hole transfer are often limiting the overall system efficiency. Therefore, we propose to study the process of electron transfer between *Rhodobacter sphaeroides* reaction centers (RCs) and Os-complex redox polymers (Os-P) using transient absorption spectroscopy. RCs and Os-P were mixed in buffered solution in different ratios with addition of electron acceptor – water soluble quinone. Results show that the electron transfer between RCs and Os-P is 3-exponential under studied conditions and the fastest lifetime is of the order of a few microseconds. It also shown that the electron transfer rate increases with higher concentration of Os-P and decreases with higher concentration of RCs. These results suggest that there are a few types of complexes between RCs and Os-P being created. Their nature is discussed.

In situ Spectroelectrochemical Investigation of a Biophotoelectrode Based on Photoreaction Centers Embedded in a Redox Hydrogel

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The field of biophotoelectrochemistry and its application in biophotovoltaics and biosensors has gained more and more attention in recent years. Knowledge of the redox potentials of the catalytically active protein cofactors in biophotovoltaic devices is crucial for accurate modelling and in discerning the mechanisms of their operation. Here, for the first time, we used spectroelectrochemical methods to investigate thermodynamic parameters of a biophotoelectrode in situ. We determined redox potentials of two elements of the system: the primary electron donor in photosynthetic reaction centers (RCs) of the bacterium *Rhodobacter sphaeroides* and osmium-complex based redox mediators that are bound to a hydrogel matrix. We observe that the midpoint potential of the primary donor is shifted towards more positive potentials in comparison to literature data for RCs solubilized in buffered water solution, likely due to interaction with the polymer matrix. We also demonstrate that the osmium-complex modified redox polymer efficiently wires the RCs to the electrode, maintaining a high Internal Quantum Efficiency with approximately one electron per two photons generated (IQE = 50±12%). Overall, this bio-photoelectrode may be attractive for controlling the redox state of the protein when performing other types of experiments, e.g. time resolved absorption or fluorescence measurements, in order to gain insights into kinetic limitations and thereby help in the rational design of bioelectronic devices. (Białek et al. 2020)

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Białek R, Friebe V, Ruff A, et al (2020) In situ spectroelectrochemical investigation of a biophotoelectrode based on photoreaction centers embedded in a redox hydrogel. Electrochim Acta 330:135190. doi: 10.1016/j.electacta.2019.135190

Ordered Mesoporous Carbons as Supports for Bimetallic Pt(Cu) Catalysts in PEMFCs

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One of the main drawbacks when using Pt catalyst in the anode of polymer electrolyte membrane fuel cells (PEMFCs) is that it is easily poisoned by CO, even at low concentrations as 1 ppm. The use of PtRu catalysts or other strategies, like air-bleeding, have shown an increase of the CO tolerance in PEMFCs [1], but limited to few ppm of CO. Another strategy has been addressed the synthesis of nanoparticles with a core-shell structure or bimetallic systems, thus reducing the amount of Pt used in the electrode and increasing its tolerance towards CO [2]. A further step would be to modify the carbon support. In this sense, carbon blacks are the most typical used, but they do not have good textural properties and thermochemical stability [3], which ultimately can be detrimental for catalyst performance. On the other hand, other carbonaceous materials, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have been tested as support for Pt(Cu) nanoparticles [4]. Furthermore, in this work, Pt(Cu) nanoparticles have been synthesized on ordered mesoporous carbons (OMC), CMK-3 and CMK-8, as they also present improved textural and electrochemical properties as compared to carbon blacks, showing promising results, as can be seen in Figure 1, where the catalyst studied depict improved activity towards CO electro-oxidation.

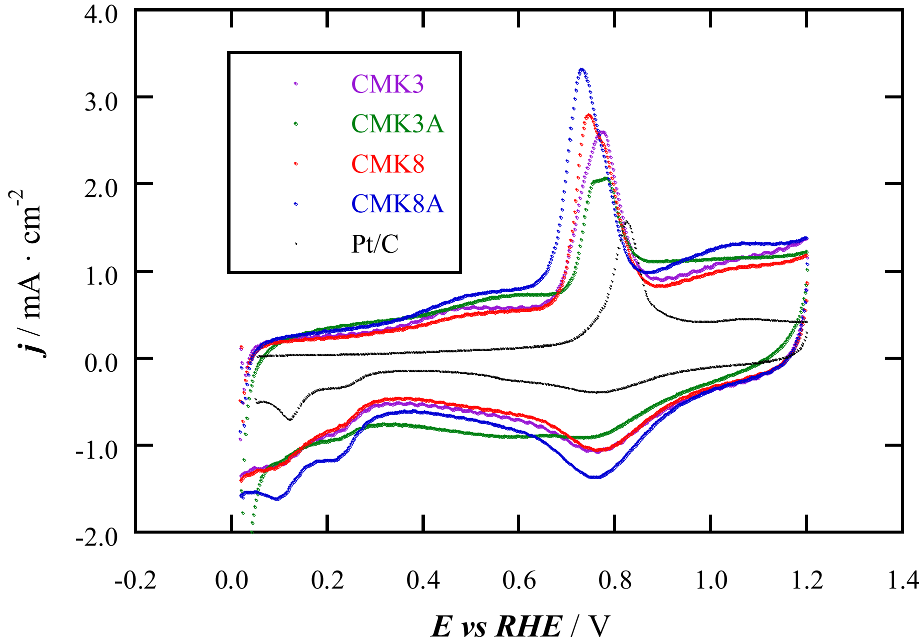

Figure 1. CO stripping curves of prepared and commercial catalysts in deaerated 0.50 M H_2SO_4 solution at scan rate of 20 mV·s^{-1}.

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EC-SERS and EC-SOERS study of 5-substituted uracil derivatives

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Surface Enhanced Raman Scattering (SERS) is a phenomenon related to the amplification of the Raman signal of an analyte interacting with a plasmonic nanostructure. This phenomenon, discovered in 1974, had a significant impact among the spectroscopy community, since it helped to overcome the main disadvantage of Raman spectroscopy: the lack of sensitivity. Recently, our group discovered a new phenomenon called Electrochemical Surface Oxidation Enhanced Raman Scattering (EC-SOERS) [1], which allows to enhance the Raman signal of an analyte during the oxidation of a silver substrate.

Although many aspects of the origin of EC-SOERS remains still unclear, this phenomenon has shown considerable potential for quantitative analysis, being used for the determination of uric acid, citric acid or acetylsalicylic acid. In one of our last works, combination of EC-SERS and EC-SOERS was used to achieve a double quantification of nicotinic acid and nicotinamide [2], a couple of analytes with great similarity between Raman spectra.

In this communication, we expose the possibility of using EC-SERS and EC-SOERS to obtain a double characterization of an analyte in a single experiment, as exposed in Figure 1. Interestingly, several shiftings and changes in the relative intensity of the bands are observed. An analysis of the spectral differences will be carried out in order to further understand the interaction between the analyte and the substrate involved in each phenomenon.

This work shows the potential to provide a highly specific double characterization of analytes in a single experiment, giving enough information to avoid interferences.

5-Substituted uracil derivatives have been studied using EC-SERS and EC-SOERS. This family of compounds have been used for many decades in chemotherapy as antimetabolite drugs and also as radiosensitizers of DNA [3,4].

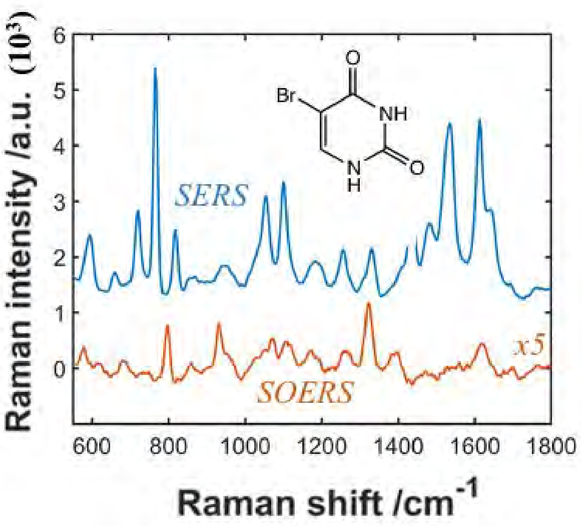

Figure 1. EC-SERS and EC-SOERS spectra of 5-Bromouracil 1mM during a time-resolved Raman spectroelectrochemical experiment.

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The dynamic nature of CO adlayers on Pt(111) electrodes

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The adlayers of CO on the Pt(111) surface are a fascinating electrochemical model system of great relevance in electrocatalysis. The potential-dependent structure and dynamics of these adlayers are complex and still controversial. While at the negative limit of the double layer potential range the presence of a close-packed (2 × 2)-3CO adlayer is well established, a coherent picture in the pre-oxidation range is still lacking.

To resolve this mystery, we here employ in situ high-speed scanning tunneling microscopy for studying the surface phase behavior in CO-saturated 0.1 M H_2SO_4 on the millisecond time scale. At potentials near the onset of CO pre-oxidation local fluctuations in the (2 × 2)-CO adlayer are observed, which increase towards more positive potentials. Above 0.20 V (vs. Ag/AgCl), this leads to an adlayer where CO_{ad} apparently reside on every top site, but still exhibit a (2 × 2) superstructure modulation. We interpret this observation as a dynamic effect, caused by a small number of highly mobile point defects in the (2 × 2)-CO adlayer. Our data indicate the coexistence of a rather static primitive (2 × 2) CO sublattice with highly dynamic CO on the residual atop sites. Density functional theory calculations support this interpretation. They show that the CO lattice near such defects relaxes into a local (1 × 1) arrangement, which can rapidly propagate across the surface. This behavior resembles the “door-opening” mechanism, which enables a high CO_{ad} surface mobility during CO pre-oxidation, even in the presence of ordered adlayers of high packing density and thus ensures effective mixing of CO_{ad} and OH_{ad} on the electrode surface.

In addition, as the potential shifts further positively, or the partial pressure of CO in the solution decreases, the above-mentioned apparent (1 x 1)-CO adlayer will be transformed into the classic (√19 × √19) R23.4°-13CO structure. The potential for transformation depends closely on the density of point defect on the surface and CO partial pressure in the solution, and there is a sort of coexistence of (1 x 1) and (√19 x √19) motives in the middle of the transition.

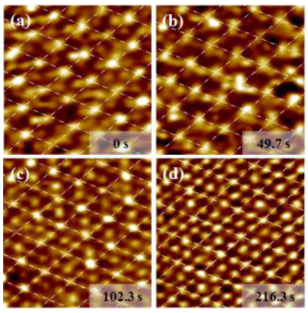

Figure 1. Potential-dependent structure of the CO adlayer on Pt(111) in CO-saturated 0.1 M H_2SO_4 solution. Video-STM images (3 nm × 3 nm) were recorded at (a) -0.10 V, (b) 0.12 V, (c) 0.20 V, and (d) 0.30 V and shoe gradual deviations from the (2 × 2) symmetry with increasing potential, resulting in a modulated (1 × 1) structure at the most positive potentials.

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J. Wei, R. Amirbeigiarab, Y.X Chen, S. Sakong, A. Gross, O. M. Magnussen. *Angew. Chem. Int. Ed.* **2020**, 59, 6182 –6186

Does the Salt Really Matter?
Impact of the Counterion Upon ECL Signal

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Typical reporting of electrochemiluminescence (ECL) mechanisms details the reactions which occur between the luminophore complex and the core electroactive structure of the target molecule. Structural similarities between ECL co-reactants have long been utilized to determine the mechanistic pathways, predict the potential regions where emission will occur and ultimately the likelihood of a species being a suitable co-reactant.[1, 2]

But what influence do the counterions have?

Counterions are vital within a range of substances but in particular within the pharmaceutical industry. Here they are utilized to improve the physiochemistry of an active pharmaceutical ingredient, ensuring the required bioavailability is obtained, by providing control over properties such as solubility, drug stability and dissolution rate. However, consideration has to date not been given to the potential impact of a target molecules counterion upon its ECL response. Traditionally considered as a bystander, counterions were not believed to bare influence upon the recorded ECL emission.

However, within this contribution we report, for the first time, how the simple change of a counterion from HBr to a HCl salt form can significantly impact upon the recorded ECL response; how this can in turn influence the reported concentrations and the significance this will have upon the wider analytical community.

Scopolamine, a pharmaceutical product and recreational drug was utilized within this proof-of-concept study. Previous work has demonstrated the suitability of scopolamine to behave as an ECL co-reactant, with the drug species successfully detected within a range of biological matrices via a basic $[Ru(bpy)_3]^{2+}$ based sensor down to clinically relevant concentrations.[3]

With both salt forms containing the identical core tropane alkaloid structure (to which their electroactivity is attributed), indistinguishable pKa values and hence comparable influence of pH toward their ECL intensity, the distinct difference observed within their obtained ECL profiles is of great interest. Direct comparison between the HBr salt and HCl salt relived differences in respect of their emission potentials and intensity. The impact of the salt form upon the ECL response has been investigated in respect of the calculated concentrations based upon the construction of calibrations curves which each salt form. Results demonstrated vastly different concentrations were obtained dependent upon the salt form within the sample and that used to produce the calibration curve. As such this bares the question of whether this phenomenon is intrinsic across all co-reactants, solely to the amine functional group or specific to scopolamine. The impact of this outcome would be of interest to the wider analytical community, and in particular forensic practitioners where electrochemical and ECL based sensors are of increasing interest. Ultimately the application of a sensor within an analytical environment relies upon its accuracy and hence a thorough understanding of such a phenomenon would only stand to widen ECL acceptance within the wider analytical community and increase its potential applications.

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Electrodeposited MnO$_2$ Nanostructures as Efficient Photocatalyst for Removal of TCs Antibiotics Pollutant

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Nowadays antibiotics are widely used not only for human and animals medicine but also as additives in feedstuff industries. Tetracycline antibiotics (TCs) are the most common antibiotics all over the world, accounting for about half of the global antibiotical production. However, TC is poorly adsorbed by animal metabolism and it is released into the environment in an active form. One of the biggest problems related to its long-term presence in water and soil is the development of antimicrobial resistance in animals which has the potentially threatens in ecosystem and human health[1]. Therefore, the global antibiotic resistance problem has reached an urgent point. Electrodeposited Manganese dioxide (MnO$_2$) has been considered as a promising photocatalyst for oxidative degradation of organic contaminants in wastewater due to its ease of synthesis, non-toxic properties, strong adsorption, strong oxidation ability, acid resistance and low-cost. However, only a few studies are available about the photocatalytic response of electrodeposited MnO$_2$ nanostructures. Besides, to the best of our knowledge, none of those studies considers the photocatalytic removal of TC pollutant. Herein, we report the synthesis of MnO$_2$ nanostructures by electrodeposition from a simple and green electrolyte bath under ambient conditions. The photocatalytic activity of MnO$_2$ was tested for the removal of TC antibiotic from water using LED visible illumination. LED lights are up to 80% more efficient and draw much less power than traditional lighting. The photocatalytic performances of the MnO$_2$ nanostructures result in an excellent photodegradation as well as an elevated percentage of mineralization of the TCs antibiotic. Besides, the photocatalyst showed good recyclability properties after performing several successive cycles, revealing its high photostability. We believe that the facile synthesis process can open up a new approach for the possible large-scale utilization of electrodeposited MnO$_2$ nanostructures as an effective visible light photocatalyst.

Figure 1: Scheme of the electrodeposited MnO$_2$ photocatalytical process for the TC removal.

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Electrochemical Dissolution of PtRu Nanoparticles: Electrocatalyst Stability During Operation and Recycling of Spent Catalysts

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PtRu alloy nanoparticles supported on high surface area carbon (PtRu/C) are common electrocatalysts used for the hydrogen oxidation reaction at polymer electrolyte membrane fuel cell (PEMFC) anodes. Recycling of these precious metals at the end of the lifetime of fuel cells is important for their further applications in a sustainable energy technology scenario. In this study,[1] we explore the electrochemical dissolution of Pt and Ru from the PEMFC anode catalyst layer, i.e., a PtRu alloy supported on carbon catalyst (PtRu/C). Effects of different dissolution routes on the relative rates of dissolution for Pt and Ru have been explored with different electrolytes, namely 0.1 M HCl and 1 M H_2SO_4. Apart from studying the effect of the presence of chloride on their stability, this study explores the electrochemical dissolution-based recovery of Pt and Ru from PtRu/C electrocatalysts. During potential cycling in presence of chloride (0.1 M HCl), the stability of Pt is observed to be lower than that of Ru. On the other hand, in absence of chloride, due to redeposition of the instable dissolved species, Pt shows stability higher than Ru. For example, the % dissolutions of Pt and Ru are observed to be ~72% and ~33% during potential cycling between 0.2 and 1.6 V for 50 cycles at a scan rate of 100 mV/s, in 0.1 M HCl. On the other hand, for similar initial Pt and Ru loadings, the corresponding dissolution values for Pt and Ru after potential cycling between 0.2 and 1.6 V for 10k cycles at a scan rate of 1 V/s in 1 M H_2SO_4 are observed to be ~27% and ~61%, respectively (Figure 1). This difference of behaviors is attributed to the formation and stability of soluble Pt and Ru species during potential cycling. The fast dissolution of Pt and higher stability of Ru found during potential cycling in dilute HCl may be explored towards separation of Pt and Ru and for separable recoveries from spent alloy catalysts.

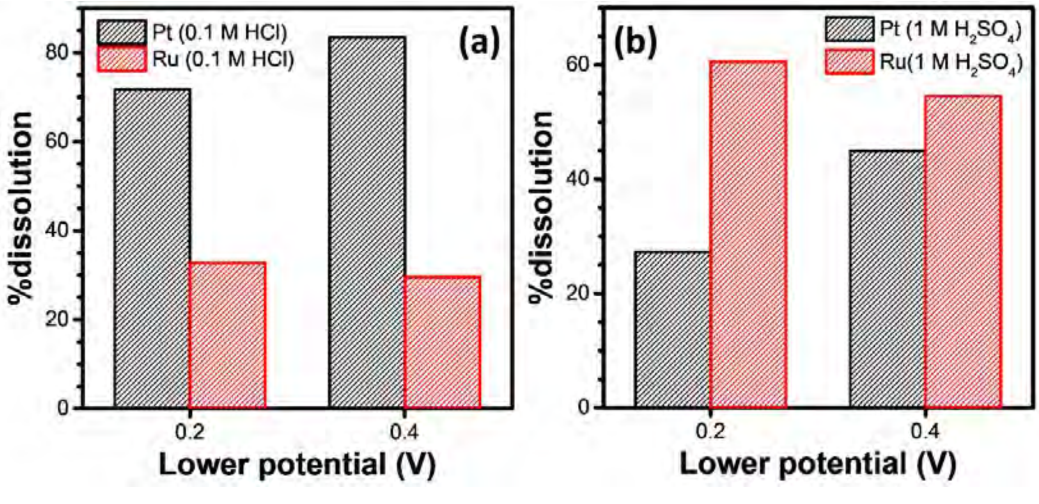

Figure 1: Variations of dissolution rate values for Pt and Ru for (a) 50 cycles between E_l and 1.6 V at a scan rate of 100 mV/s in 0.1 M HCl and (b)10000 cycles between E_l and 1.6 V at a scan rate of 1 V/s in 1 M H_2SO_4), for two different E_l values of 0.2 and 0.4 V.

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Effect of Plasma Electrochemical Treatment of Boron Doped Diamond on the Electron Transfer Kinetics of Model Redox Reactions

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Due to the high stability of sp^3 carbon towards active intermediates, boron doped diamond (BDD) is utilized as an electrode material in electrochemical devices for wastewater purification from toxic and not easily biodegradable organic ecopollutants. However, a drawback of BDD is a relatively low rate of electron transfer (ET) which limits the productivity of such systems. In the present study, the effect of plasma electrochemical treatment of BDD surface on the ET rate of outer and inner sphere electrode reactions was studied by the example of model redox systems.

A typical electrode used in the study was a 10–20 μm thick boron doped diamond film on a silicon substrate. ET rate constants were assessed on the basis of the data of cyclic voltammetry carried out in 5 mM $K_3[Fe(CN)_6]$ + 1 M Na_2SO_4, 5 mM $[Ru(NH_3)_6]Cl_3$ + 1 M Na_2SO_4 and 5 mM $FeSO_4$ + 0.25 M H_2SO_4 solutions on the initial and treated BDD electrodes. The electrode surface was treated in 1 M Na_2SO_4 solution as a result of ca. 20 impulses of anodic plasma generated at 300 V [1]. The rate constant of outer sphere electron transfer in the case of $Ru^{3+/2+}$ was determined not to depend on the state of BDD surface and equals ca. 10^{-2} $cm^2 \cdot s^{-1}$. For inner sphere electron transfer ($[Fe(CN)_6]^{3-/4-}$ and $Fe^{3+/2+}$), in contrast, the ET rate is sensitive to plasma electrochemical treatment. Namely, after electrode treatment with the anodic plasma impulses, the rate constant decreases from 10^{-3} $cm^2 \cdot s^{-1}$ to 10^{-4} $cm^2 \cdot s^{-1}$ for $[Fe(CN)_6]^{3-/4-}$ and increases from $5 \cdot 10^{-7}$ $cm^2 \cdot s^{-1}$ to ca. $3 \cdot 10^{-6}$ $cm^2 \cdot s^{-1}$ for $Fe^{3+/2+}$ which is considered to be the most sensitive to the surface state. The data of X-ray photoelectron spectroscopy demonstrate the increase in concentration of oxygen-containing functional groups on the surface of BDD after its plasma electrochemical treatment. Thus, such an effect of BDD electrode treatment on the electron transfer kinetics should be explained by the functionalization of boron doped diamond surface with oxygen-containing groups, which affect the rate of considered model redox reactions in a different way.

The study was carried out in the framework of the State Assignment no. AAAA-A19-119061890019-5 of 18.06.2019 using the equipment of the Multi-User Analytical Center of IPCP RAS and the equipment of the Multi-User Center of Scientific Center in Chernogolovka RAS.

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Iron (II) phthalocyanine on nanostructured carbon as electrocatalyst for oxygen reduction in Microbial Fuel Cells

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Abstract

Microbial fuel cells (MFCs) are a versatile platform that aims at harvesting electricity by using the electrons coming from organic waste degradation catalysed by microorganism metabolism. However, challenges, such as high cost and low durability of electrode materials, lead to the use of platinum at the cathode side, limiting the applicability of MFCs [1]. To overcome this issue, low cost catalysts based on non-noble metals were developed demonstrating promising catalytic activity toward oxygen reduction reaction (ORR) [2]. Platinum-group-metal-free (PGM-free) are mostly based on transition metals supported on nitrogen-containing carbon matrix [2,3]. In this context, we propose novel catalysts based on FeN4 macrocycles supported on nanostructured carbon spheres (Fe-N-C), for direct oxygen reduction to water in neutral environment. A facile three-step-method of synthesis was developed to obtain Fe-N-C catalysts, were Iron (II) phthalocyanine (FePc) and urea (CH_4N_2O) were used as iron and nitrogen source, respectively, and carbon black pearls (BP) as carbon support. Figure 1 shows a flowchart of the synthesis strategy, together with a schematic of ORR mechanism and performance at a surface of a typical Fe-N-C catalyst. Structural, morphological and electrochemical properties of catalysts were investigated, and the set of results indicated that Fe-N-C catalysts have a good catalytic activity towards ORR in neutral pH, thanks to their high surface area and density of active sites which make them suitable for MFC applications.

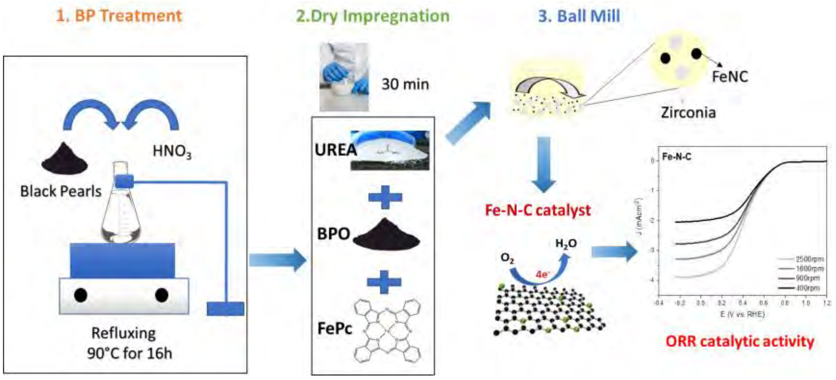

Figure 1. Schematic illustration of Fe-N-C catalyst production and its electrochemical performances via hydrodynamic linear sweep voltammogram.

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Ion–Solvent Chemistry in Alkali Metal Batteries

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Alkali metal batteries are considered as promising next-generation energy storage devices due to their ultrahigh energy densities. However, the high reactivity of alkali metal toward organic solvents and salts renders inevitable side reactions, which further leads to undesirable electrolyte depletion, cell failure, and evolution of flammable gas. Ion–solvent chemistry was proposed to prove the intrinsic instability of normal organic electrolytes towards alkali metal anodes through multiscale calculations (density functional theory (DFT) calculations, ab initio molecular dynamics (AIMD) simulations, and in situ microscopic observations. Once complexed with cations in electrolytes, solvent molecules exhibit a significantly reduced the lowest unoccupied molecular orbital (LUMO) energy level, facilitating the electrolyte decomposition and gas evolution. The origin of such phenomenon can be explained by two mechanisms in ether and ester electrolytes, respectively. The LUMO energy levels of ion–ester complexes exhibit a linear relationship with the binding energy, regulated by the ratio of carbon atomic orbital in the LUMO, while LUMOs of ion–ether complexes are composed by the metal atomic orbitals. AIMD simulations further prove the electrolyte decomposition kinetics on alkali metal anodes. The broken of C–O bond in electrolyte solvents is always accompanied by the formation of Li/Na–O bond, validating the role of coordinated cations in promoting electrolyte decomposition. In situ optical microscopic observations validated the theoretical predictions that electrolyte gassing on Li/Na metal surface is obviously promoted after introducing cations into electrolytes.

Based on the proved ion–solvent chemistry, several strategies were proposed to build stable electrolytes for alkali metal anodes, including additive design and regulating anions in electrolyte solvation shell. Both electrolyte additives and anions from salts can participate electrolyte solvation of cations and regulate the composition and structure of solid electrolyte interphase (SEI). More importantly, a fancy strategy of cation additive was proposed as different cations have a different impact on solvent molecules. Three principles, including the LUMO energy level decrease of solvents after coordinating with cations, the electrode potential of introduced cations in electrolytes, the binding energy between cations and solvents, were proposed to select proper cation additives for sodium metal batteries. Besides, the role of electrolyte solvation in regulating ion–solvent interactions was also systematically investigated. The cation additive strategy affords emerging chances for rational electrolyte design for stable and safe Na metal batteries and also affords a fresh research paradigm for other batteries.

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Effect of Complex Formation on Mass Transfer during Metal Electrodeposition on Rotating Disk Electrode

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При электросаждении металлов и сплавов достаточно широко используются растворы, содержащие комплексы ионов металла с отрицательно заряженными лигандами [1]. Процессы массопереноса в растворах с комплексами включают гомогенные химические реакции и потоки лигандов, возникающие при восстановлении комплексов, что позволяет существенно повысить эффективность электрохимических процессов за счет реализации электро- и автокатализа, эффекта экзальтации. Известно, что электромиграция может значительно увеличить значение предельной плотности тока в случае электровосстановления катионов из растворов, содержащих комплексы, а при определенных условиях предельный ток может вообще отсутствовать [2]. При теоретическом анализе массопереноса в условиях комплексообразования обычно используются упрощенные математические модели (приближение диффузионного слоя Нернста, условие равновесия реакции комплексообразования, равенство коэффициентов диффузии всех компонентов), что в ряде случаев позволяет получить приближенные аналитические решения [3]. Очень часто приближения, принятые в упрощенных математических моделях, не выполняются: ионы имеют существенно отличающиеся значения коэффициентов диффузии, наряду с электродиффузионным осуществляется и конвективный перенос компонентов, реакция комплексообразования является неравновесной, что может оказывать существенное влияние на закономерности массопереноса в условиях комплексообразования. В связи с этим представляет интерес исследование влияния гидродинамических условий, транспортных свойств и скорости гомогенной химической реакции на процессы переноса в условиях комплексообразования, которое можно выполнить только с использованием численных методов [4].

In this work the effect of complex formation on the mass transfer during the metal electrodeposition on a rotating disk electrode from the solution containing three types of ions (metal cation, cationic complex and non-electroactive anion) is studied theoretically. The dimensionless Nernst-Planck equations in the approximation of solution electroneutrality, which take into account the electro-diffusion and convective transfer of all types of ions and the homogeneous reaction of complex formation, are used as the mathematical model. The Butler-Volmer equations are used to take into account the kinetics of electrochemical reactions. In contrast to the known works, the approximations of the Nernst layer, equality of the diffusion coefficients of all types of ions, and the equilibrium of complex formation reaction were not used. As a result of numerical solution, the distributions of concentration, potential, and the rate of complex formation reaction are obtained at various parameters of the system under consideration. It is shown that the constants of the equilibrium and rate of complex formation reaction, as well as the ratio between the diffusion coefficients of complex cation and anion have the strongest effect on the mass transfer.

The work was performed with support of Ministry of Science and Higher Education of Russian Federation. The study was partially funded by Russian Foundation for Basic Research and Tula region, project no. 19-48-710008.

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Ultrafine Pt nanoparticles supported on double-shelled C/TiO_2 hollow spheres material as highly efficient methanol oxidation catalysts

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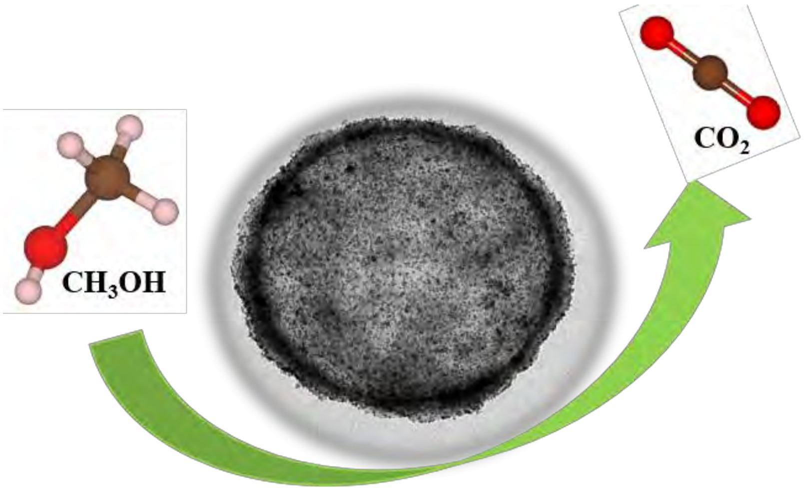
Abstract

Catalyst support is extremely important for future fuel cell devices. In this work, we developed double-shelled C/TiO_2 (DSCT) hollow spheres as an excellent catalyst support via a template-directed method. The combination of hollow structure, TiO_2 shell and carbon layer results in excellent electron conductivity, electrocatalytic activity, and chemical stability. These uniformed DSCT hollow spheres are used as catalyst support to synthesize Pt/DSCT hollow spheres electrocatalyst. The resulting Pt/DSCT hollow spheres exhibited high catalytic performance with a current density of 462 mA mg^{-1} for methanol oxidation reaction, which is 2.52 times higher than that of the commercial Pt/C. Furthermore, the increased tolerance to carbonaceous poisoning with a higher I_f/I_b ratio and a better long-term stability in acid media suggests that the DSCT hollow sphere is a promising C/TiO_2-based catalyst support for direct methanol fuel cells applications.

Keywords: Catalyst support; C/TiO_2 hollow sphere; Metal-support interactions; Methanol oxidation reaction



Graphical abstract

Modeling of Electrodeless Electrochemical Nanoprinting

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Local electrodeposition (LED) is one of effective methods for formation of 3D micro- and nanostructures. It exhibits several important advantages: the absence of mechanical and heat impacts on the workpiece, no tool wear, wide possibilities for controlling the shape of microstructures by varying machining modes, low cost of electrochemical processes, and good reproducibility of results [1]. Electrodeposition is particularly unique in its ability to create deposit at sub-nanometer vertical resolutions [2]. Various schemes of maskless local electrodeposition are used: jet LED, scanning probe based LED and micro/nanopipette based LED (electrochemical micro/nanoprinting). At present, the schemes of LED using unipolar or bipolar electrodes [3, 4], are widely used, whereas the electrodeless LED remains almost unstudied.

This work is devoted to the theoretical analysis of electrodeless electrochemical nanoprinting using a nanopipette filled with the electrolyte solution more concentrated than the bulk solution. The external potential is not imposed onto the conductive substrate, and there are no other electrodes. As a result of different solution concentrations near the substrate, cathodic and anodic zones form on it. Local metal deposition from the solution occurs on the cathodic zone near the nanopipette, and anodic dissolution of substrate metal occurs on the large anodic zone on the periphery of electrochemical cell. The ionic transport equations, which take into account diffusion, migration, and convection, and the condition of electroneutrality, are used as the mathematical model. The boundary conditions on the substrate are set using the Butler-Volmer equation. The numerical solution of the problem is carried out by the finite element method on the deformable grid that takes into account the change of the substrate surface shape due to the local deposition and dissolution of metal.

As a result of simulation, the distributions of ion concentrations and potential over the solution, and the distributions of current density, overpotential, and concentration of electroactive ions over the substrate surface are obtained for various time instants and under various conditions.

The work was performed with support of Ministry of Science and Higher Education of Russian Federation. The study was partially funded by Russian Foundation for Basic Research and Tula region, project no. 19-48-710008.

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Cyclic Voltammetry of Homogeneous Autocatalytic Reduction of Iodate on Rotating Disk Electrode

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Voltammetry is widely used in the study of electrode reaction mechanisms that involve homogeneous chemical processes coupled to electron transfer [1]. Теория cyclic voltammetry of homogeneous redox catalysis of electrochemical reactions достаточно хорошо разработана и позволяет выразить (описать) the cyclic voltammetric responses as functions of two dimensionless parameters: a kinetic parameter, and an excess factor [2]. Одним из частных, но весьма важным, случаем электрокатализа является гомогенный автокатализ (так называемый CE’’ механизм [3]) при котором количество катализатора увеличивается в ходе процесса. Упрощенно механизм гомогенного автокатализа может быть представлен следующей схемой (k>1):

$$A \pm e^- \leftrightarrow M$$

$$M + S \rightarrow kA + \text{products}$$

Этот механизм реализуется при электрохимическом восстановлении иода (который присутствует в растворе в весьма малой концентрации) с образованием iodide, и последующим the reduction of iodate by iodide (known as the Dushman reaction) [4]. В работе [5] показано, что the catalytic reduction of iodate at a rotating platinum disk electrode has been employed to study the kinetics of the reaction between iodate and iodide и при использовании ряда упрощений получено a closed form solution for the catalytic current.

Настоящая работа посвящена теоретическому исследованию процессов переноса при of homogeneous autocatalytic reduction of iodate on rotating disk electrode (RDE). В качестве математической модели использованы нестационарные уравнения ионного переноса, учитывающие диффузию, миграцию, конвекцию и гомогенные химические реакции, а также условие электронейтральности. Кинетика электрохимической реакции учитывалась с помощью уравнения Батлера-Фольмера. Численное решение осуществлялось методом конечных элементов на нерегулярной сетке, что обеспечивало высокую эффективность и требуемую точность численного решения.

В результате численного моделирования получены зависимости формы и параметров voltammograms от концентрации раствора, скорости развертки потенциала и скорости вращения RDE. Установлено, что при достаточно больших скоростях развертки потенциала пиковое значение тока окисления существенно больше пикового значения тока восстановления. Это объясняется тем, что при больших скоростях развертки потенциала за время изменения потенциала от наибольшего до наименьшего значений (точно не знаю, как сказать – прямой ход, изменение потенциала в катодную область и т.д.) не успевает образоваться достаточно большого количества iodide.

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Comparison between microporous layered and non-layered GDLs; Experimentally validated in terms of gas transport and performance in membrane fuel cells

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Gas diffusion layers (GDLs) used in membrane fuel cells are widely recognized as a critical component that largely contributes to its performance. Essentially, properties of GDLs are known to vary significantly, depending upon manufacturing techniques employed [1-2]. Recently, many advances have been made in GDLs with an addition of a microporous layer (MPL) on the substrate layer to facilitate water management by preventing water infusion and disallowing surface wetting. This work aims at comparing an MPL layered (34 BC) with a non-layered (34 BA) GDL from SIGRACET by ; (i) ex situ gas transport measurement in which GDLs were stacked in 25cm^2 cell to measure equivalent gas permeability (in terms of viscous permeability and inertial permeability), [1-2] and (ii) electrochemical performance. Results showed a higher viscous permeability by 5 times for 34 BA due to larger pore sizes and the absence of MPL compared to 34 BC. From the polarization curves, 34 BC with lower gas transport capability, showed reasonably decent performance specifically at a higher current density of 0.8 A/cm^2, indicating sufficient control towards water management. In 34 BA, however, which was prone to flooding led to pore blockage, and overall gas transport was compromised, as a consequence early decline was seen at a current density of 0.4 A/cm^2 [1].

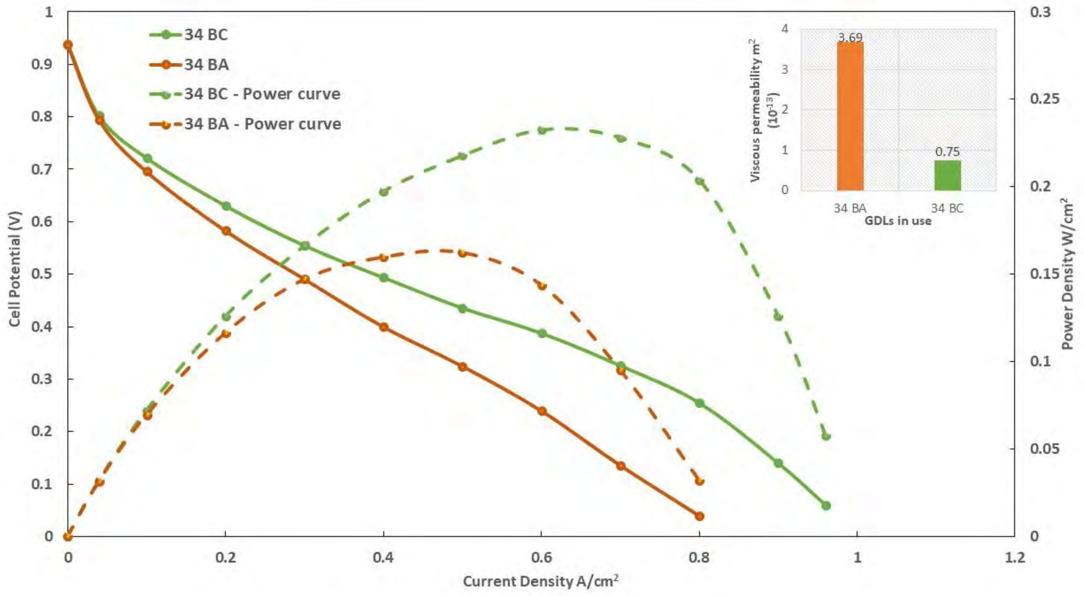

Figure 1. The performance curves on the selected GDLs and viscous permeability values

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Simulation of Electrochemical Micromachining by Nanosecond Voltage Pulses

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Electrochemical micromachining (ECMM) with using nanosecond voltage pulses between a tool electrode and a workpiece enables one to form complex-shaped three-dimensional structures with submicrometer precision[1]. The principle is based on the dependence of double-layer charging time on the interelectrode gap (local separation between the electrodes). This results in a highly localized region for electrochemical dissolution or deposition. This technique is used for local anodic dissolution of various metals and silicon as well as for local metal electrodeposition.

The accuracy and productivity of ECMM depends significantly on the operating conditions, in particular, on the interelectrode gap, the pulse-on time and pulse frequency. The pulse-on time can be estimated using an approximate equation for the time constant for electric double layer charging [1]:

$$\tau = CS/\sigma \tag{1}$$

Here C is the specific capacity of electric double layer; S is the interelectrode gap; and σ is the conductivity of electrolyte solution.

The results of modeling and the experimental data [2, 3] give much lower times of double-layer charging. This complicates choosing appropriate machining mode.

In this work, the transport processes in the electrolyte solution and charging-discharging of electric double layer are analyzed theoretically. As a result, an approximate analytical equation for the time constant for double-layer charging is obtained:

$$\tau = \frac{2RTC}{nFi_{\mathrm{F,SS}}} \ln \frac{i_{\mathrm{F,SS}}}{i_0} \tag{2}$$

Here, $i_{\mathrm{F,SS}}$ is the Faraday current density for the charged electric double layer; i_0 is the exchange current density; *n* is the number of electrons involved in the electrochemical reaction; *R* is the gas constant; and *T* is the temperature.

The results of numerical calculations agree well with the approximate analytical equation (2).

Thus, the proposed model of electrochemical micromachining by nanosecond voltage pulses can be used for justified choice of pulse-on time in ECMM.

The work was performed with support of Ministry of Science and Higher Education of Russian Federation.

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Acid-Base Electrochemical Flow Battery using Neutralization Energy

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The development of clean, renewable, and affordable energy sources as a consequence of the global warming has become a necessity for society. Consequently, is highly required the development of devices capable of efficiently storing the energy obtained from these sources. In this sense, Hydrogen-based technologies have become a promising candidate both as fuel and transmission element. [1].

A redox flow battery is an electrochemical energy storage device that converts chemical energy into electrical energy through reversible oxidation and reduction of working fluids [2]. Based on this concept an Acid-Base Electrochemical Flow Battery (ABEFB) has been developed. This system is composed of acidic and alkaline solutions, both with a high supporting electrolyte concentration, which are separated by a cationic exchange membrane. Hydrogen oxidation and evolution reactions take place during the charge and discharge processes, which acidifies or basifies the corresponding electrolytes. The neutralization energy obtained from these solutions is used as electromotive force [3]. In this case, HCl and NaOH are used as electrolytes, NaCl as supporting electrolyte, a platinised Pt electrode as cathode, a Pt-catalysed gas diffusion electrode as anode (catalyst loading of 0.5 mg cm^{-2}) and a cationic membrane as ionic separator.

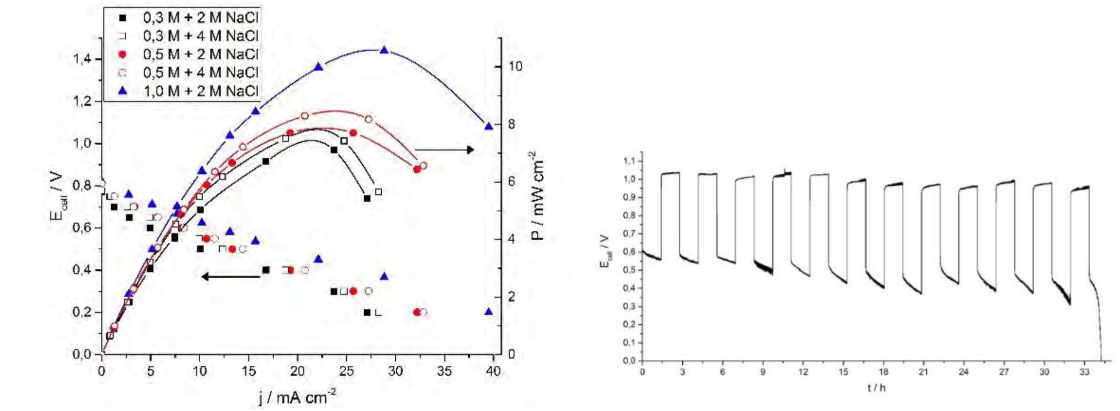

Figure 1:a) Polarization curves and power curves for 0.3, 0.5 and 1.0 M HCl/NaOH, with 2.0 and 4.0 M NaCl. b) Charge/discharge cycles for a charge capacity of 3350 mAh, at 12.5 mA cm^{-2}

In this work, the effect of the supporting electrolyte concentration, the state of charge, and the nature of cationic membrane have been systematically studied. Polarization curves and charge/discharge cycles were obtained to evaluate the performance of the system. We found that this battery can provide a maximum power density of 10.6 mW cm^{-2} at 27.5 mA cm^{-2}, and a coulombic efficiency of around 80 %, depending on the H^+/Na^+ ratio and the membrane thickness. This study reveals a promising energy-storage system, with simple operation and low cost.

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Lithium Bonds in Lithium Batteries

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Lithium bonds are analogous to hydrogen bonds and are therefore expected to exhibit similar characteristics and functions. Additionally, the metallic nature and large atomic radius of Li bestow the Li bond with special features. As one of the most important applications of the element, Li batteries afford emerging opportunities for the exploration of Li bond chemistry.

In this work, we have briefly summarized the historical development of the Li bond. Especially, the similarities and differences between the Li and H bonds were discussed. Subsequently, the Li bond was described in the context of Li batteries, including discussions of sulfur cathodes, liquid electrolytes, and Li metal anodes. Such discourse on the chemistry of the Li bond can provide fruitful insight into the fundamental interactions within Li batteries and thus deliver a deeper understanding of their working mechanism. In this way, a comprehensive understanding of the Li bond in Li batteries and an outlook on its future developments is presented.

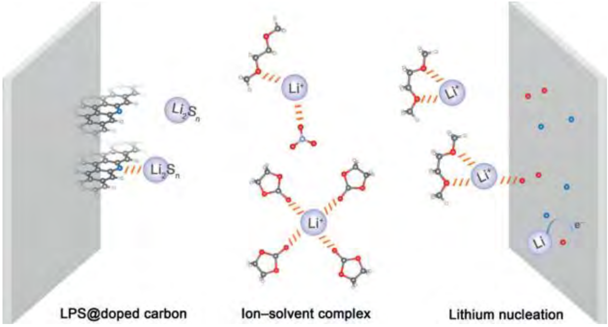

Figure 1. Schematic representation of the Li bond in Li batteries. LPS: Lithium polysulfide.

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Automated Investigation of Cyclic Voltammetry Data

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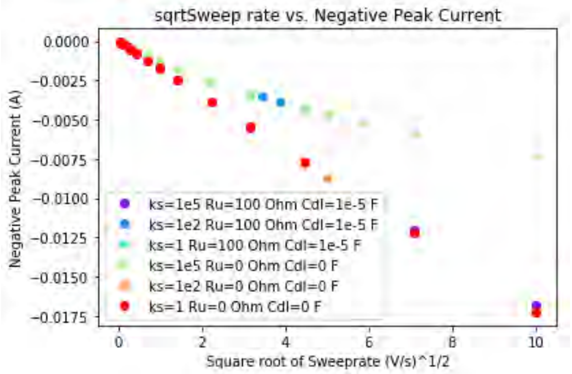
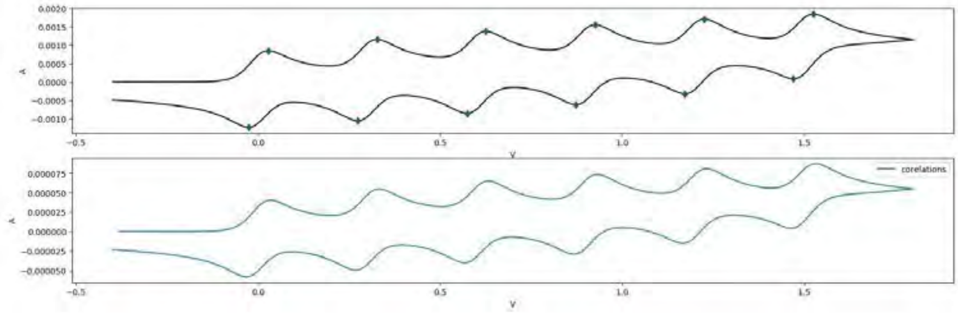
Cyclic voltammetry has been a powerful and versatile tool for every modern electrochemist. It is straightforward to use and can easily grant information on the many properties of the system it is used on.

Interpretation of the cyclic voltammetry data is traditionally done via sweep rate dependence of parameters such as anodic and cathodic peak currents and the separations of the said peaks. A standalone automated system that can do electrochemical analysis requires autonomous detection of electrochemical signals. The idea of autonomous electrochemistry was first introduced by John Arthur Eklund in his thesis supervised by Larry Faulkner. At the time, the experiment used was chronocoulometry and not much progress was made afterwards.

To date, algorithms for finding electrochemical peaks and their respective baselines have used various methods that require many parameters from the operator and/or locate critical points in the data externally. These methods either require human input in real time, or during design time in the form of thresholds. This is mostly due to the potential large noise in the data that may blur the peak locations or baseline locations.

To remedy those problems we have developed a versatile software using Python Programming Language, "AutoCV", which locates the positions of peaks and their respective baselines on the data using little to none operator input while accounting for the noise and artifacts in the data. In order to account for noise and artifacts we have developed a method in which we use the correlation function between an "ideal peak" generated from the work of Nicholson & Shain and noisy data which yields finely clarified peaks and diminished noise and artifacts. Then using these information "AutoCV" can determine many things including; reduction and oxidation peak positions (even if there is more than 1 of each), whether the system is stable or not, whether there are any coupled chemical reactions or not or kinetics of the electrode. Also, in a given set of data it can detect if there is a peak separation and whether it is due to kinetic reasons or not. If the cyclic voltammetry data is inadequate satisfy wanted confidence for the inquisition of the property, software will suggest another experiment to further analyse the property in question. This software is easily modifiable, and its parameters can be adjusted to obtain wanted properties of the system with desired confidence. Also, it can easily be updated to analyse data from many different techniques and do analysis on all the data at the same time.





Tailoring the permeability of chitosan-based coatings deposited on zinc substrates with different methods

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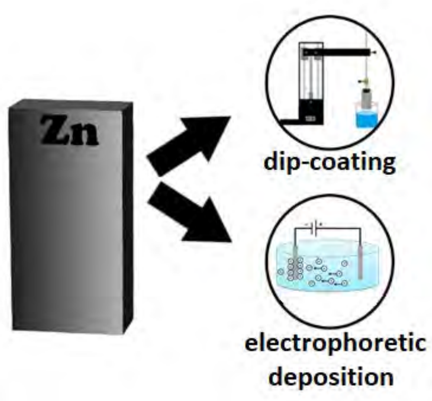
Chitosan is a highly versatile biopolymer, with applications in various domains, including medicine, agriculture and the packaging industry [1]. Recently, the use of chitosan as an anticorrosive barrier was also studied [2, 3].

Depending on the substrate nature, chitosan can be applied to a surface as a protective coating by multiple techniques. Conventional methods, such as dip-coating have a high success rate due to the simplicity and reproducibility of the coatings [4]. In the case of metal substrates, however, electrophoretic deposition can also yield good results [5].



Our study aims to tailor the permeability of chitosan coatings through different deposition techniques and impregnation/accumulation of additives which could act as corrosion inhibitors. As such, different types of chitosan-based coatings were deposited on zinc substrates and studied mainly through electrochemical methods (electrochemical impedance spectroscopy and potentiodynamic polarization).

The obtained results highlight that in the case of dip-coating, thin, native chitosan layers do not offer any significant protection (in some cases, even a slight reduction of impedance was noted). These highly permeable thin layers can be crosslinked, or used as accumulation matrices, resulting in high corrosion inhibition efficiencies of >90%, suggesting reduced permeability. On the contrary, thick chitosan layers produced from highly viscous solutions can provide some reduced amount of protection (*ca.* 30%), but, due to the thickness of the polymer barrier, in these cases, an effective modification through crosslinking proved to be impossible.

Electrophoretic deposition was an ineffective method in the case of zinc substrates, possibly due to the presence of $ZnO/Zn(OH)_2$ on the metal surface, hindering the production of a uniform layer (proven through microscopy). Electrochemical measurements show a decent inhibition efficiency in these cases, however, due to the non-uniform coverage, leading to increased probability of pitting corrosion, this method was deemed inappropriate for zinc substrates.

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Density Functional Theory Analysis of Structural and Electronic Properties of NASICON-structured $Na_xTi_2(PO_4)_3$ (x = 1 – 4)

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Sodium-ion batteries represent an alternative to current generation of lithium ion batteries due to higher sustainability and potentially lower cost. However, there is still a lack of suitable electrode materials especially on the negative electrode side. Na SuperIonic CONductor (NASICON) type systems demonstrates are among the leading candidates for Na-ion battery applications [1,2]. In the present study, first principles calculations within the linear combination of atomic orbitals and Gaussian basis set formalism were employed in order to study the structural an electronic structure peculiarities in $Na_xTi_2(PO_4)_3$ compounds with different degrees of sodiation (x = 1-4). Hybrid exchange-correlation functionals (HSE06 and B1WC) were used to investigate the band gap changes for different x [3]. We identified the Ti oxidation states and correctly predicted the mixed oxidation state (mixed valence) for x = 2 and 4. Moreover, the mixed oxidation states showed smaller band gaps by ~0.6 eV for x = 2 and 4 vs. 4.1 and 2.2 eV for x = 1 and 3, respectively (Fig. 1). We discuss the nature of this effect based on the analysis of electronic density of states. We demonstrate important role of the electroneutrality condition to find the ground state for each x. Finally, a correlation was found between the bulk electronic properties of $Na_xTi_2(PO_4)_3$ compounds and the symmetry changes due to the variation of sodium content and accompanying charge ordering. The calculations of phonon frequencies at the Γ-point revealed no presence of imaginary frequencies for the ground state structures. These structural peculiarities for $Na_xTi_2(PO_4)_3$ compounds are suggested to have an important effect on their performance in battery applications such as the electrochemical kinetics and polaronic charge transport.

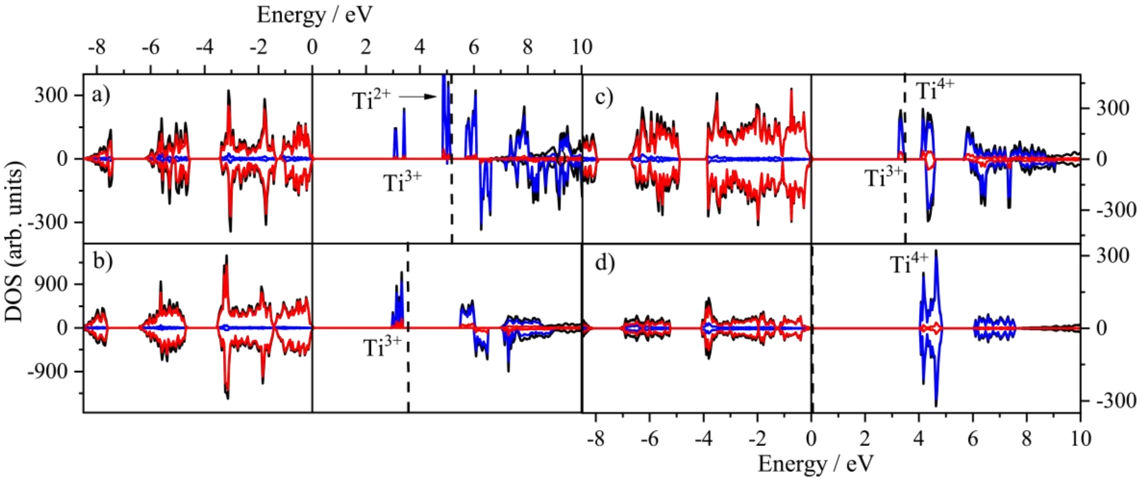

Fig. 1. Electronic Density of States (DOS) for NaxTi2(PO4)3 where (a) x = 4, (b) x = 3, (c) x = 2, (d) x = 1. The Fermi energies are marked by dashed lines.

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Layered manganese-based oxides as cathode materials for sodium ion batteries

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Benefiting from natural abundance and wide distribution of sodium sources, sodium ion batteries (SIBs) demonstrate promising application prospects in hybrid electric vehicles and large-scale energy storage.[1] The capacity of cathode materials is, however, mainly provided by the redox reactions of metal ions, which is difficult to be further improved.[2] Significantly, incorporating a certain amount of lithium ions into the transition metal layer of layered manganese-based oxides can stimulate anionic redox reactions, thus realizing higher capacity.[3] Although layered manganese-based oxides are promising to break through the capacity bottleneck of cathode materials, their capacity and output voltage tend to drastically decay. Therefore, it is imperative to put forward new strategies to stabilize the anionic redox reactions.

In this work, we introduced inactive zinc ions into the sodium layer to synthesize the zinc-doped Na$_{5/6}$[Li$_{1/4}$Mn$_{3/4}$]O$_2$ (NLMO-Zn). A new phase was generated when the undoped sample (NLMO) were charged to the high voltage zone through in situ XRD to observe the phase evolution of zinc-doped and undoped samples during charging and discharging. Interestingly, the NLMO-Zn always maintained single-phase reaction (Fig. a and b), indicating that the Zn-doping could effectively inhibit the phase transformation at high voltage. The charge compensation mechanism analysis of the two samples based on photoelectron spectroscopy (XPS) and X-ray absorption near-edge spectroscopy (XANES) characterization illustrates that NLMO-Zn displayed higher Mn^{4+} content after cycling compared with NLMO (Fig. c). Moreover, the first principles theoretical calculation revealed that the zinc-doped samples had more stable intermediates and lower phase transition probability under different sodium content states (i.e. different charge and discharge states). This doping strategy effectively inhibits the Jahn-Teller effect of Mn^{3+} and avoids phase transition, thus stabilizing the anion redox reaction and greatly improving the electrochemical properties. This study offers considerable application potential toward the development of high-energy SIBs.

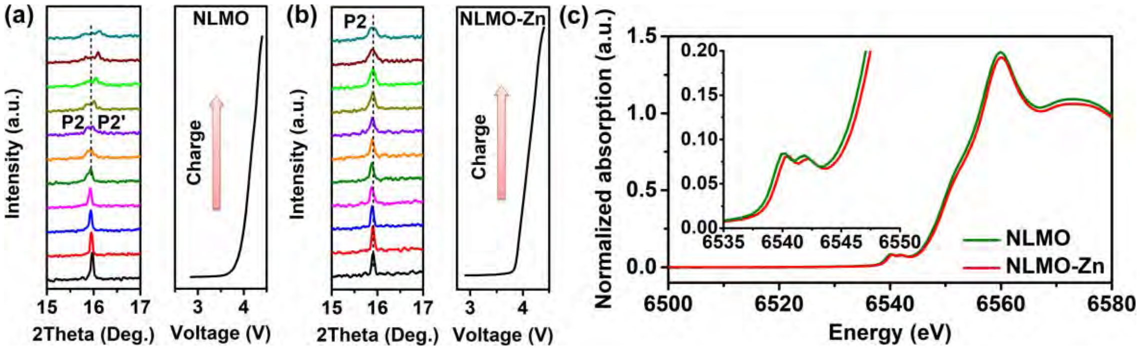

Figure. In situ XRD patterns of NLMO (a) and NLMO-Zn (b) during the 1st charge and the XANES spectra at the Mn-K edge for NLMO and NLMO-Zn at the fully charged states (c).

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Ultrafine Fe_3O_4 nanoparticles immobilized on two-dimensional Ni-based metal-organic framework for enhanced oxygen evolution reaction

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Construction of inorganic-organic hybrid nanostructures with elaborate design is a promising strategy for advanced oxygen evolution reaction (OER) electrocatalysts with earth-abundant elements. Herein, we have successfully synthesized ultrafine Fe_3O_4 nanoparticles homogeneously immobilized on two-dimensional Ni based metal organic frameworks (MOFs) (Fe_3O_4/Ni-BDC). The functionalized Fe_3O_4 nanoparticles (diameter: 6 ± 2 nm) with abundant surface hydroxide groups are initially fabricated by hydrothermal method, and then anchored on two-dimensional (2D) Ni-BDC layers (thickness: 5 ± 1 nm) with strong non-covalent interactions through a sonication process. The obtained Fe_3O_4/Ni-BDC composites inherit the superior surface structure and physicochemical features of 2D Ni-BDC layers. Meanwhile, the introduction of Fe_3O_4 simultaneously modifies the integral electronic structure and prevents the aggregation of 2D Ni-BDC for enhanced OER performance. In contrast, a mechanically mixed control group shows unmodified electronic structure and unsatisfying activities. We have investigated electronic structure and morphology changes for different amounts of Fe_3O_4 immobilized on the Ni-BDC layers, by a wide range of techniques including XRD, FT-IR, XPS, SEM, AFM and TEM. The optimized Fe_3O_4/Ni-BDC-4 composite demonstrates significantly enhanced OER performance with an overpotential of 295 mV at 10 mA cm^{-2}, a Tafel slope of 47.8 mV dec^{-1} and a superior operational stability for more than 40 h. Furthermore, the reaction mechanism and the valance state of metals species related to OER performance are carefully studied.

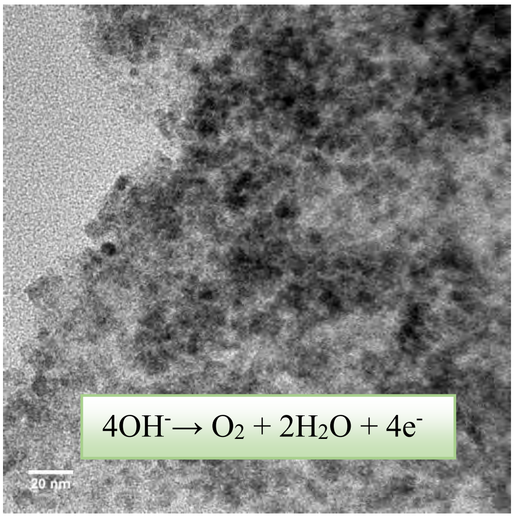

Figure 1. TEM image of the Fe_3O_4/Ni-BDC-4 composite; Inset is the overall reaction for OER.

Paenibacillus dendritiformis within alginate polymer covered graphitized paper with artificial or self-developed redox network

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Recently, we developed redox-active Ca-alginate polymer for fast immobilization of the Gram-negative bacteria *Pseudomonas putida* [1]. In the present study, we entrapped a Gram-positive strain *Paenibacillus dendritiformis* MA 72, which was proved to form electrochemically active biofilms. Before inoculation and polymerization of the gel, a mixture of 1 mM thiazolyl blue (MTT) formazan/phenazine methosulfate (PMS) was added to form an artificial redox network. The presence of the redox couple was observed on the DPV as a well-defined peak at a potential of -0.05 V (vs. SHE) with a distinguishable Faradaic current in the presence of bacteria, while the abiotic control showed a twice higher capacitive current (Fig.1a). In the absence of redox dyes, no peaks have been observed in the beginning. The polymer covered bioelectrodes (±dyes as additives) have been continuously poised at −0.195 V, and their electrochemical behavior was investigated. The current density in the presence of the redox couple was 6 times higher during the first 70 h, but after ca. 170 h the current of both bioelectrodes became equal (Fig.1b). The registered peak on the DPV suggests that the bacteria have developed a self-produced redox matrix within the alginate which is sensitive to different applied potentials (Fig.1c), indicating that diverse bacterial surface or mobile molecules contact with the electrode and participate in the bacterial response.

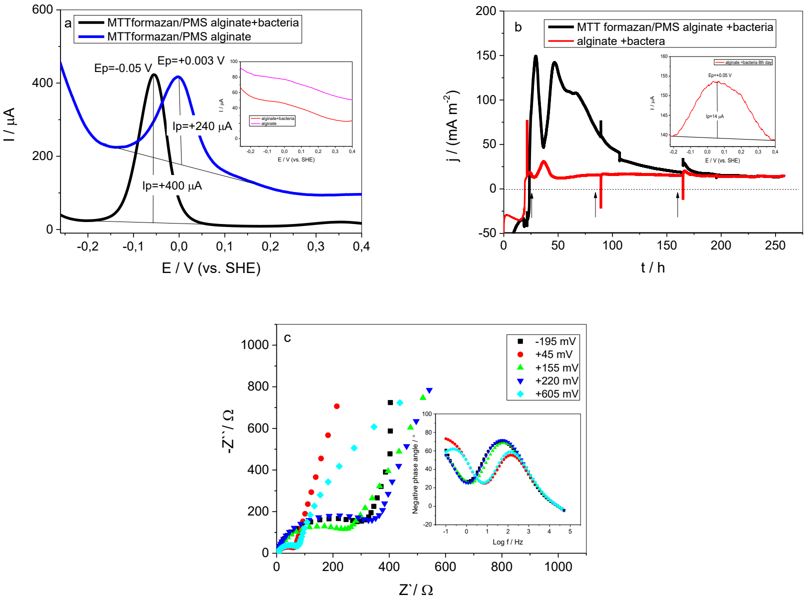

Fig. 1. a) DPV in the beginning; b) Current density generated at −0.195 V applied potential. Inset - DPV of the alginate polymer sample on the 8th day; c) EIS- Nyquist plot of the alginate polymer sample on the 8th day, 50 kHz-15mHz, ac signal 10 mV, different Edc. Inset – the corresponding Bode plot.

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Electrochemical Impedance Spectroscopic Investigation on the Solvation/Desolvation Processes of Lithium Ions at SEI/Electrolyte Interfaces of Lithium Metal Anode

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The existence of solid-electrolyte interphase (SEI) on the surface of lithium metal is a prominent feature that distinguishes it from other metals, which also inevitably exacerbates the complexity of Li electrodeposition compared to traditional metal electrodeposition at solid/liquid interfaces. Li metal as anode is actually composed of Li (or current collector)/SEI/electrolyte interfaces. Accordingly, Li metal electrodeposition starts always from the desolvation of Li ions at the SEI/electrolyte interface, which is then followed by transportation of Li ions through the SEI to the metal/SEI interface for discharge. Therefore, the SEI and its coupling interfaces in bridging the substrate and electrolyte play key roles, and their structures and properties could directly affect the electrodeposition behaviors of Li metal.

Herein, by adopting the strategy of controlled construction of SEI and metal/SEI/electrolyte interfaces, the investigation by electrochemical impedance spectroscopy (EIS) was carried out to systematically study the processes on Li metal electrodes, especially focusing on the solvation/desolvation processes of Li ions at the SEI/electrolyte interface. First, various kinds of smooth and uniform SEIs with adjustable structure and thickness were fabricated on Li metal and Cu substrates using electrochemical polishing-based method recently proposed by the authors' group[1,2], the well-defined SEI/electrolyte interfaces facilitating accurate EIS analysis. Then, potential-dependent EIS were performed to study the solvation/desolvation kinetics in the electrolyte of LiTFSI/DME-DOL. Meanwhile, the influence of $LiNO_3$ additive was also investigated. Results show that the thickness of SEI and its chemical composition in the outer layer, determining the structures and properties of the SEI/electrolyte interface, significantly affect the solvation/desolvation of Li ions. Our work are beneficial to the understanding of the metal/SEI/electrolyte interfaces and their roles in the solvation/desolvation of Li ions.

This work was supported by the Projects of National Natural Science Foundation of China (21972119, 21673193) and the Postdoctoral Science Foundation of China (2019TQ0177).

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Investigation on Methanol Tolerance of Pt/C Cathode Catalyst with Heteroatom-doped Carbon Layer for Direct Methanol Fuel Cell

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Direct methanol fuel cell (DMFC) is one of the most commercialized technology in direct liquid fuel cells due to various advantages of rapid refueling and high energy density, which are crucial characteristics for portable applications. DMFC consists of methanol oxidation reaction at anode and oxygen reduction reaction (ORR) at cathode on PtRu-based and Pt-based catalyst, respectively. Most challenging problem toward DMFC is methanol crossover. Methanol at the anode permeates the cathode and reacts with cathode catalyst, resulting in voltage drop. Pt/C is an excellent catalyst, but it actively reacts with methanol at the cathode. Thus, it is crucial to design a methanol-tolerant Pt-based catalyst to increase the ORR selectivity at the cathode.

In this study, we synthesized Pt/C with heteroatom-doped carbon layer. Heteroatom-doped Pt/C showed both lower activity in the methanol oxidation reaction and higher activity in ORR than pristine Pt/C. The origin of selectivity will be investigated with electrochemical tests such as CO stripping voltammetry and XPS in aspects of oxophilicity and Pt electronic structure. Finally, we will apply heteroatom-doped Pt/C on the cathode and confirm selectivity compared with pristine Pt/C. This approach suggests the way to design a Pt catalyst for ORR to improve performance in DMFC.

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CO_2 Electroreduction at $Pt_{0.8}Ru_{0.2}/C$ in a Polymer Electrolyte Membrane Electrolyzer Cell

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Recently, CO_2 reduction is one of the most interesting topics in the field of electrochemistry. There are many reports on the CO_2 electroreduction at transition metal electrodes such as a Cu electrocatalyst.[1] In our previous study, we have proposed an approach that uses a polymer-electrolyte based single cell containing a Pt/C electrocatalyst, which enabled to reduce CO_2 without overpotential. Remarkably, we have demonstrated that CO_2 is reduced to CH_4 with a high efficiency and high selectivity by diluting the CO_2 concentration to be fed.[2,3] Also, we have revealed that the efficiency of CH_4 generation was $Pt/C < Pt_{0.5}Ru_{0.5}/C < Pt_{0.8}Ru_{0.2}/C$ when 100 vol.% CO_2 was supplied.[4] Hence, it is expected that more efficient CH_4 production from CO_2 reduction will be realized by combining the techniques of diluting the CO_2 concentration and using a $Pt_{0.8}Ru_{0.2}/C$ electrocatalyst. In this study, we investigated the stationary-potential CO_2 reduction on a $Pt_{0.8}Ru_{0.2}/C$ under a reduced CO_2 concentration.

We prepared a polymer electrolyte cell equipped with a Nafion®-based membrane electrode assembly containing the 42.5 wt% $Pt_{0.8}Ru_{0.2}/C$ and 45.7 wt% Pt/C as the working and counter electrodes (WE and CE), respectively. Fully humidified H_2 and Ar/CO_2 (CO_2 concentration: 7 vol.%) were supplied to the CE and WE, respectively. Cell temperature was 40°C. The experimental setup in this study is drawn in Fig. 1. The WE potential was stepped from 0.4 V to 0.2 V. After 300-s holding, the potential was stepped to 0.05 V. During the procedures, in-line mass spectrometry (MS) was conducted to analyze the products in real time. All the potentials are shown with the reference to reversible hydrogen electrode (RHE).

Fig. 2 shows MS signals of *m*/*z* 2 (for H_2) and 15 (for CH_4) with applied potential program. The signal of *m*/*z* 15 is observed and almost constant under the potential holding at 0.2 V. On the other hand, the signal of *m*/*z* 2 is observed only after stepping the potential to 0.05 V. Significantly, the faradaic efficiency between 240 s and 299 s for $Pt_{0.8}Ru_{0.2}/C$ was calculated to be 18.2%, which exceeds the efficiency for Pt/C (12.3% at 0.16 V).[3] Overall, this work revealed that the continuous CH_4 production from CO_2 reduction with a high efficiency without overpotential or H_2 evolution was achieved using the $Pt_{0.8}Ru_{0.2}/C$ electrocatalyst under a reduced CO_2 concentration.

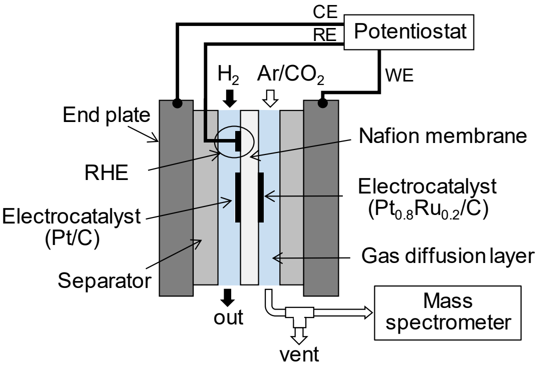

Fig. 1. Schematic diagram of the experimental setup in this study.

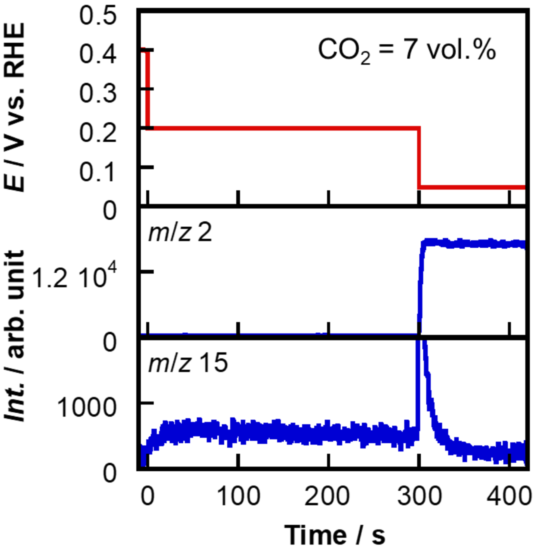

Fig. 2. Potential program applied to the working electrode and MS signals (*m*/*z* 2 and 15) measured simultaneously at $Pt_{0.8}Ru_{0.2}/C$ by feeding 7 vol.% CO_2 at 40°C.

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A Diffusion−Reaction Competition Mechanism to Tailor Lithium Deposition for Lithium Metal Batteries

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These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated. Li metal is recognized as one of the most promising anode materials owing to its ultrahigh theoretical specific capacity and low electrochemical potential. Nonetheless, Li metal anode has been severely hindered from practical applications by dendritic Li growth. The uncontrollable Li dendrites can result in low Coulombic efficiency (CE) and short cycle life of a working battery. More seriously, the Li dendrites penetrate the separators and reach the cathode to cause internal short-circuits, which even leads to thermal runaway and explosions. However, the continuous conversion between Li metal and Li ions implies the inevitable existence of Li deposition during the plating step. Accordingly, the key to suppress the Li dendrite growth is to tailor Li deposition.

Compared to available deposition morphologies of Li metal anode, spherical Li deposition endows two important merits from its unique morphology. Firstly, spherical Li deposition features well-defined morphology with smooth surface without any sharp tip, thus avoiding serious safety hazards caused by dendritic Li deposition. Secondly, Li sphere exhibits minimum surface area per unit volume among all the other morphologies, which signifies higher CE and longer cycle life because of forming few solid electrolyte interphase (SEI) by the reaction between fresh Li and electrolyte. Many researches have focused on regulating Li deposition into spherical shapes. However, the underlying mechanism of forming Li spherical deposits has not been clarified yet. If the fundamental rationale behind different morphologies of Li deposition can be unveiled, it is conceivable that safe Li metal batteries can be further achieved based on tailoring Li deposition morphology.

In this work, we report a diffusion−reaction competition mechanism which can determine the ion concentration beneath the SEI and therefore tailor the morphology of Li deposition. When maintaining the same electrode reaction rate, through modifying the kinetics of Li diffusion from slow to fast, the ratio of sphere/all deposition (including spherical and dendritic Li) (denoted as S/D) continuously rises due to the progressively higher Li ion concentration beneath SEI. Changing the electrode reaction rate is found to alter the Li plating morphology, since higher reaction rate can induce ion depletion within SEI. This work provides a deep, fundamental understanding of Li deposition morphology that guides the design of future strategies to enable dendrite-free Li deposition.

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A Diffusion−Reaction Competition Mechanism to Tailor Lithium Deposition for Lithium Metal Batteries

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Graphene Quantum Dots/Gold Nanostructure Chiral Composite for Enantiomeric Sensing

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The investigation of chiral compounds has a fundamental significance for understanding the intrinsic properties of the biomolecular building blocks and chemical processes occurring in living organisms. Because of this, the enantioselective detection of chiral species is crucial in drug discoveries, pharmaceuticals and biochemical processes. It is well established that the contrary enantiomers of chiral compounds often differ significantly in their pharmacological, toxicological and pharmacokinetic properties. Previous researches have demonstrated that electrochemical enantioselective sensors have been attracted significant attention owing to various advantages over spectrophotometric and chromatographic techniques. By introducing chirality by organic moieties into solid inorganic materials creates local chiral environments for enantiosensing. Therefore, it is our main objective to investigate the interaction between L-/D-proline with gold nanorods (AuNRs)/graphene quantum dots (GQDs) in order to explain their effect in detecting the racemic mixture. The exceptionally high specific surface area, high conductivity, fast electron transfer kinetics and good biocompatibility of AuNRs and GQDs have attracted attentions from various fields, including biological ones. Due to the simple one-step pyrolysis of citric acid and L-/D-proline to obtain chiral proline-functionalized GQDs and electrostatic self-assembly interaction between negatively charged GQDs and positively charged AuNRs, it is worth exploring the potential of this nanohybrid material as sensing material during fast sweep voltammetry. The characterization of this nanohybrid material was carried out by electrochemical, morphological and spectroscopic techniques. The electroanalysis of chiral compounds by the nanohybrid-modified electrode was studied thoroughly by electrochemical method and its molecular chiral recognition mechanism was modeled by molecular docking method. Successful investigations have produced a new nanohybrid material that suitable as a chiral sensor in nanodevices. The outcome from this research has led to important implications for biosensing, asymmetric syntheses and separation, and significant understanding on the nature of chiral interactions in biological systems.

Earth-Abundant Coal-Derived Carbon Nanotube/Carbon Composites as Efficient Bifunctional Oxygen Electrocatalysts for Rechargeable Zinc-Air Batteries

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The exploration of active and robust electrocatalysts for both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is the bottleneck to realize the commercialization of rechargeable metal-air batteries and regenerative fuel cells. Here we report facile synthesis of three-dimensional (3D) carbon nanotube (CNT)/carbon composites using earth-abundant coal as the carbon and heteroatom dopant source to grow CNTs. The prepared composite featuring 3D structural merits and multiple active sites can efficiently catalyze both ORR and OER, affording high activity, fast kinetics, and long-term stability. With the additional incorporation of manganese, the developed catalyst afforded an overvoltage of 0.80 V between ORR at the half wave potential and OER at the current density of 10 mA cm^{-2}. The optimized sample has presented an excellent OER performance within a constructed solar-energy water splitting device with continuously generating oxygen bubbles at anode. Notably, it can be further used as a durable air-electrode catalyst in constructed Zn-air battery, delivering an initial discharge/charge voltage gap of 0.73 V, a remained voltaic efficiency of 61.2% after 160 cycles and capability to power LED lamps for at least 80 hours. This study provides an efficient approach for converting traditional energy resource i.e. coal to value-added alternative oxygen electrocatalysts in rechargeable metal-air batteries.

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Electrochemical CO_2 Reduction to Multi-carbon in Continuous-flow CO_2 electrolyzer

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Use of electrochemical method for reduction of carbon dioxide (CO_2) convert into valuable organic compounds, is a great solution to solve the problem of CO_2 accumulation. The most advantage of electrochemical conversion is to elect reaction to produce a few organic compounds from carbon dioxide depending to types of catalyst. Among many types of catalyst, metal catalysts based on Copper element or alloy metals offers the route to synthesize multi-carbon fuels and chemicals from CO_2 (*e.g.*, ethylene, ethanol and n-propanol).

In this study, Copper Phosphide was determined by one of the candidate to solve the problem and it was synthesized by oleate method and used as a catalyst in a near Zero-gap CO_2 gas-phase electrolytic cell for CO_2 reduction reaction at ambient temperature and pressure. By using a hydrophobic gas diffusion layer (GDL), exhibited the formation of three-phase boundary during the CO_2 reduction reaction. The mechanism of the reactions, verified by the onset point of CO and other oxygen-bounded intermediates adsorption with ATR-SEIRAS, *in-situ* surface analysis, which is the intermediate of most products by CO_2 reduction reaction. Headspace GC-MS, UV-Vis, NMR equipment was used to verify gas/liquid product analysis. Their results show that multi-carbon fuels, such as C_4 products, acetaldehyde are produced.

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The morphological change of Ni/C electrochemical catalyst for hydrazine oxidation

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Hydrazine fuel cell is one of the promising liquid fuel cells due to its high theoretical voltage, high energy density, and no emission of green gas. However, hydrazine can decompose chemically or electrochemically as a function of the type of catalyst used. Despite being a precious metal, platinum is an ambiguous catalyst because of faradaic reaction catalyst of hydrazine as well non-faradaic reaction. Therefore, in terms of the fuel efficiency, platinum is not suitable for hydrazine oxidation catalyst. Nickel, which is in the same family as platinum, is non-precious metal, and due to its similar structure to platinum, it performs greatly against hydrazine oxidation. In these aspects, hydrazine fuel cells are even more important, not requiring the expensive noble metal. Here, we synthesized Ni nanoparticles via polyol method by changing the type of Ni precursor, since chemical, physical, and electro-chemical properties of a metal nanoparticle depend on its morphology and size. When using nickel nitrate, the size of the Ni nanoparticles is the smallest, amorphous morphology, whereas when using nickel chloride, the size is slightly larger, but the particles spread well on carbon support. Then, in order to confirm hydrazine electro-oxidation reaction, catalyst ink was loaded on the rotating disk electrode (RDE), and cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out.

Precise Anionic Regulation of NiFe Hydroxysulfide Assisted by Electrochemical Reactions for Efficient Electrocatalysis

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Highly efficient electrocatalysts with high intrinsic activity for oxygen and sulfur redox reactions are strongly required for sustainable energy systems. Generally, cations serve as the real active sites in transition metal compound electrocatalysts, whose electrocatalytic activity is regulated by the surrounding anionic structure. Herein, an electrochemical reaction assisted by an anionic regulation strategy is proposed for precise construction of advanced electrocatalysts with extraordinary electrocatalytic activity. The electrochemical anionic regulation process ensures general release of the regulation reagents for precise substitution of sulfur anions in pristine hydroxide. The as-obtained hydroxysulfide electrocatalyst exhibits a desired electronic structure to afford superb electrocatalytic activity regarding reduced overpotential of 286 mV at 10 mA cm^{-2} for electrocatalytic oxygen evolution and improved polysulfide redox electrocatalytic activity. This contribution not only renders an emerging strategy for precise regulation of the anionic structure for improved electrocatalytic activity, but also provides information for the rational design of advanced electrocatalysts for sustainable energy applications.

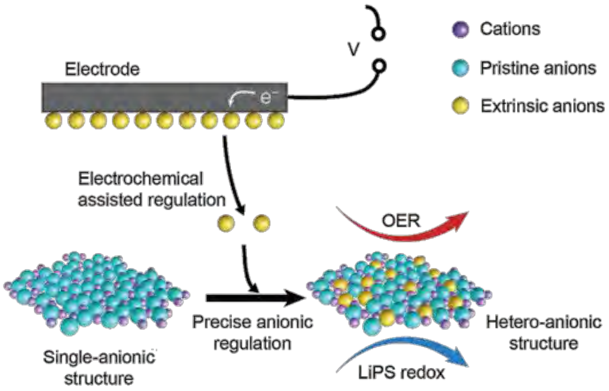

Fig. 1 Schematic of the precise anionic regulation assisted by electrochemical reaction for enhanced electrocatalytic activity.

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Multiscale Construction of Bifunctional Electrocatalysts for Long-Lifespan Rechargeable Zinc–Air Batteries

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Zinc–air batteries deliver great potential as emerging energy storage systems but suffer from sluggish kinetics of the cathode oxygen redox reactions that render unsatisfactory cycling lifespan. The exploration on bifunctional electrocatalysts for oxygen reduction and evolution constitutes the key solution, where rational design strategies to integrate various active sites into a high-performance air cathode remain insufficient. Herein, a multiscale construction strategy is proposed to rationally direct the fabrication of bifunctional oxygen electrocatalysts for long-lifespan rechargeable zinc–air batteries. NiFe layered double hydroxides and cobalt coordinated framework porphyrin are selected as the active sites considering their high intrinsic activity at the molecular level, and the active sites are successively integrated on three dimensional conductive scaffolds at mesoscale to strengthen ion transportation. Consequently, the multiscale constructed electrocatalyst exhibits excellent bifunctional performance ($\Delta E = 0.68$ V), which is even better than the noble metal based benchmarks. The corresponding air cathodes endow zinc–air batteries with a reduced voltage gap of 0.74 V, a high power density of 185.0 mW cm^{-2}, and an ultralong lifespan of more than 2400 cycles at 5.0 mA cm^{-2}. This work demonstrates a feasible strategy to rationally integrate various active sites to construct multifunctional electrocatalysts for energy-related processes.

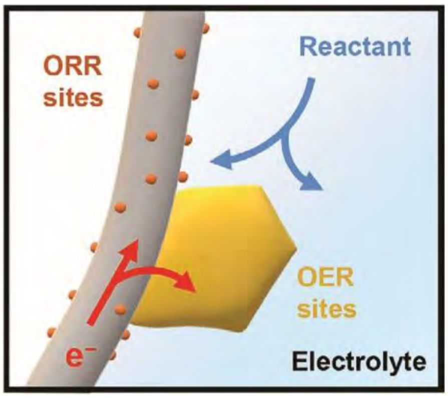

Fig. 1 Schematic illustration of the multiscale construction strategy.

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Cascade reactions by nanoconfinement of intermediates for electroreduction of CO_2

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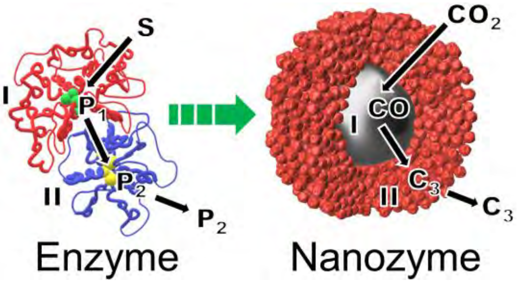

Enzymes can produce highly complex molecules with high efficiency because of their ability to perform cascade reactions via substrate channelling. Using substrate channelling, two different active sites can be connected via a tunnel that allows the diffusion of intermediates to the next active site without diffusion to the bulk solution. Mimicking the architectural features of enzymes in electrocatalytic nanoparticles, called nanozymes, is an approach we have previously applied to single step reactions[1,2] and now seek to apply to cascade reactions.

Electrochemical CO_2 reduction is a suitable model reaction for cascade reactions, given it can be divided into two steps with CO as the key intermediate.[3] In this work, we designed an electrocatalytic nanoparticle, called a cascade nanozyme, comprising a Ag core, where CO_2 can be reduced to CO, and a porous Cu shell, where CO is further reduced to more complex organic molecules.[4] Cascade nanozymes were synthesised and characterised for electrochemical CO_2 reduction using GC and ^{1}H-NMR. We were able to demonstrate a cascade reaction with C_3H_8O formed at -0.6 V vs. RHE on the cascade nanozymes, where experimental controls containing exclusively Cu showed no activity for C_3 products.[4]

Operando TEM, applied for the first time to CO_2 reduction, was used to visualise the electrocatalytic nanoparticles in electrochemical CO_2 reduction conditions. Control experiments were conducted in a variety of conditions to help elucidate the processes. It was found that applied potential and (local) CO concentration had the greatest impact upon structural evolution. This understanding was used to design and synthesise PdCu cascade nanozymes, with a lower rate of CO production and increased stability.

This work demonstrates the capacity of catalytic nanoparticle architecture to confine intermediates from one active site to another in cascade reactions. In electrochemical CO_2 reduction, such substrate channelling can create high local concentrations of important intermediates like CO. We have found that such high local concentrations can enhance the selectivity for longer chain hydrocarbons and influence structural stability, illustrating the trade-off between activity, selectivity and stability that must be considered.

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Ni-Fe Hydroxide/Oxide Nanostructures generated on Stainless Steels for Efficient Alkaline Water Electrolysis

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Developing highly active and durable electrocatalysts for oxygen evolution reaction (OER) have been needed for efficient hydrogen generation by electrochemical water splitting. Various transition metal-based oxides, hydroxides, etc. have been extensively explored as OER catalysts for alkaline water electrolysis (AWE) [1]. Recently, Stainless steels (SS) have much attractive attentions as low-cost, highly active and stable electrode materials at high current density [2]. However, relation between nano-level structures of the surface oxide layers on the SS substrate and OER properties should be clarified. In this study, we investigated changes in OER properties and nanostructures of the surface oxide layers generated on the 316SS electrode during the electrolysis.

316SS (ø = 5mm, t = 4mm) substrate was used as a working electrode after the surface polishing by Emery papers and alumina paste. Polarization curves for the OER with a disk rotation rate of 1600 rpm were measured in N_2-purged 1 M KOH solution at 75 °C at 5 mV/sec. Cyclic voltammograms were collected at 50 mV/sec without disk rotation. After that, constant current density electrolysis (CCE) was conducted at 30 mA/cm^2 for 10 h at 1600 rpm. Nanostructures and compositions of the surface (hydro)oxide layers generated after the electrolysis were investigated by scanning transmission electron microscopy (STEM) with electron dispersive spectroscopy (EDS).

Fig.1 (a) shows changes in the OER overpotentials estimated by the polarization curves at 10 and 100 mA/cm^2 as a function of the CCE times. The overpotentials decreased with increasing the CCE times. In addition, as shown in (b), the cyclic voltammograms indicate the Ni-oxidation peaks of the CCE-5h sample shift to lower potential compared with the pristine substrate (CCE-0h), suggesting the surface electrochemical property of the SS changed during the electrolysis. STEM images of the CCE-5h sample with different magnifications are presented in (c). The surface (hydro)oxide films are composed of 20 nm-thick dense buffer layer (substrate side) and 60 nm-thick nanofiber-like layers. The selected area electron diffraction (SAED) patterns suggests that crystal structures of each (hydro)oxide layers are rock-salt NiO and $Ni(OH)_2$, respectively. Furthermore, corresponding STEM-EDS mappings reveals that Fe and Ni are only metal elements and Cr is almost absent in both the oxide layers. Therefore, increase in OER activity during the CCE probably stems from generation of the specific Ni-Fe hydroxide nanostructures that acting as highly-OER-active sites [3]. The results in this study clearly show that electrochemical synthesis of such the hetero-structured hydroxide/oxide layers on the SS substrate is an effective approach for developments of the practical anode for AWE [4].

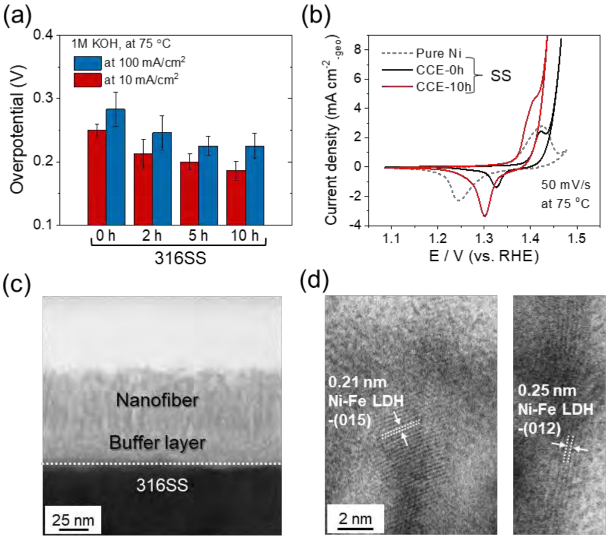

Fig.1 (a) OER overpotentials of 316SS as a function of CCE times. (b) Cyclic voltammograms of CCE-0h, and -10h samples. STEM images (c) and (d) of the CCE-5h sample [4].

Acknowledgments

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Selective CO_2 Electroreduction to Ethylene and Multicarbon Alcohols via Electrolyte-Driven Nanostructuring and Plasma Activation

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The electrochemical production of fuels and chemicals from CO_2 and water using electricity derived from renewable energy holds promise as a sustainable process that might help to mitigate some of our current energy and climate challenges [1,2]. The CO_2 electroreduction reaction (CO_2RR) is a complicated catalytic process due to the broad range of products that can be obtained at high overpotential. Multicarbon oxygenate and hydrocarbon products (C_{2+}) with high energy density are highly desirable, but severely limited by the slow kinetics of multiple proton and electron transfer steps during C-C coupling. Cu is the only metal able to produce hydrocarbons and alcohols in considerable amounts. However, polycrystalline Cu usually suffers from the need to employ high overpotentials and its low C_{2+} product selectivity. The formation of C_{2+} products during CO_2RR is very sensitive to the catalyst structure [3,4]. It is desirable, therefore, to develop nanostructured electrocatalysts through rational design that could be capable of efficient generation of multicarbon products from CO_2RR.

Surface reconstructions are commonly observed in heterogeneous catalysis, with the most active catalysts dynamically adjusting to the electrolyte, applied potential and other reaction conditions [5-9]. In this work, an efficient electrochemical strategy has been developed, namely, electrolyte-driven nanostructuring, for the synthesis of high surface area nanostructured Cu catalysts for the selective generation of C_{2+} products from CO_2RR [10]. Chlorine-modifications lead to the growth of Cu nanocubes on the polycrystalline Cu surface, while iodine-modifications produce needle-like Cu structures. Interestingly, the newly-created rough Cu catalysts show a suppressed methane formation but improved CO_2RR selectivity towards ethylene and multicarbon alcohols as compared to the flatter pristine Cu foils. The iodine-modified Cu catalyst displays the highest Faradaic Efficiency of ~80% for C_{2+} products at -0.9 V vs RHE. Operando high energy resolution fluorescence-detected X-ray absorption near edge structure (HERFD-XANES) spectra show that some Cu(I) species can still survive in the form of Cu-halide and/or Cu_2O at the negative potentials relevant to CO_2RR. It provides direct evidence of the positive correlation between the presence of Cu(I) species during CO_2RR and improved C_{2+} production. We further study the relative role of Cu oxidation state versus morphology/facet in the case of Cu nanocubes (chlorine-modified Cu) using a low temperature plasma technique [11]. The Cu oxidation state and morphology can be tuned by O_2-, H_2- and Ar-plasma pretreatments. Of them, O_2-plasma treatment destroys the Cu(100) facets of Cu nanocubes but stabilizes Cu^+ species as revealed by quasi in situ XPS developed by our group. Our results demonstrate that the presence of oxygen species in surface and subsurface regions of the Cu nanocube catalysts is key for achieving high activity and hydrocarbon/alcohol selectivity, even more important than the presence of Cu(100) facets.

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Molecular origin of negative component of Helmholtz capacitance at electrified Pt(111)/water interface

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Electrified solid/liquid interfaces are the key to many physico-chemical processes in a myriad of areas including electrochemistry and colloid science. Despite tremendous efforts devoted to this topic, it is surprising that molecular level understanding of electric double layers is still lacking. In particular, it is perplexing why compact Helmholtz layers often show bell-shaped differential capacitances on metal electrodes, as this would suggest a negative capacitance in some layer of interface water. I will present our latest ab initio molecular dynamics simulations of electrified Pt(111)/water interfaces, aiming at unraveling the structure and capacitive behavior of interface water. Our calculation reproduces the bell-shaped differential Helmholtz capacitance, and for the first time shows that the interface water follows the Frumkin adsorption isotherm when varying the electrode potential, leading to a peculiar negative capacitive response. Our work provides valuable insight into the structure and capacitance of interface water, which can help understand important processes in electrocatalysis and energy storage in supercapacitors.

Hybrid Co_3O_4@CoS nanoparticles in a N/S-doped carbon matrix as An Efficient Bifunctional Electrocatalyst for Oxygen Reduction and Evolution Reactions in Zn-Air Battery

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The development of high-performance non-precious bifunctional electrocatalysts for both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) is urgently needed to realize the commercialization of rechargeable metal-air battery. Herein, we report a ZIF-67 derived hybrid Co-based carbon composite bifunctional ORR/OER electrocatalyst exhibiting excellent performance and stability in a custom-built Zn-air battery. The catalyst was formed by pyrolytic carbonization of ZIF-67 followed by mild oxidation and sulfurization to a hybrid composite comprised of multiple active sites including Co-N_4, Co-N/S-C, C-N/S-C, Co_3O_4 and CoS, as well as the surface and edge defects in the carbon matrix, that act concertedly yielding a highly efficient bifunctional ORR/OER catalyst for reversible oxygen electrodes. The catalyst affords remarkably low reversible overpotentials and stability not only in a 3-electrode system, but also in a custom-constructed Zn-air battery, exhibiting competitive performance against benchmark bifunctional ORR/OER electrocatalysts reported to-date and thus placing it among the best non-precious metal catalysts for reversible oxygen reactions.

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The Influence of Iron, Aluminum and Manganese Impurities on the All-Vanadium Redox Flow Battery Performance

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Vanadium redox flow batteries (VRFB) are a rapidly emerging technology for grid scale energy storage and the integration of the renewable energy generation. However, the cost of the electrolyte is a major barrier for implementation of VRFBs [1, 2]. The quality of the electrolyte has a significant impact on the cell performance and cost [1-4]. Thus, understanding the impact of the impurities present in electrolyte on the performance of VRFBs is vital for commercialization of VRFBs [5]. This paper aims to conduct a systematic study on the effect of iron, aluminum and manganese ions (Mn^{2+}, Fe^{2+} and Al^{3+}) on the performance of VRFBs.

A three-electrode system was utilized to conduct cyclic voltammetry (CV) experiments. The battery performance was evaluated in a flow cell using a 'zero-gap' cell design with an electrode area of 5 cm^2. The electrolyte solution (1 M $VOSO_4$ in 3 M H_2SO_4) was circulated through the cell.

The CV results indicate that the rate of side reactions increase with the concentrations of the metal impurities. Comparison of the effect of three transition metal ions (Mn^{2+}, Fe^{2+} and Al^{3+}) showed that the highest VO^{2+} / VO_2^+ peak separation was obtained in the presence of Fe^{2+}. The VO^{2+} / VO_2^+ peak separations for $Mn^{2+}$and Al^{3+} were almost the same. The battery performance over 50 cycles with 0.1 M of each metal was compared at a range of current densities. The highest energy efficiency was observed with the pure electrolyte. Based on the cyclic voltammetry results, the kinetics of the vanadium reaction falls, and the peak separation increased with increasing concentration of the contaminant metal ions Al^{3+}, Mn^{2+}, and Fe^{2+}. The energy efficiencies have the same trend and illustrates that the contaminant metal ions are competitive with vanadium ions for adsorption on the electrode surface and thus affect the vanadium redox reaction kinetics [6]. The side reactions caused by the metal ions can also have a negative influence on the performance of VRFBs.

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Hybrid Co_3O_4@CoS nanoparticles in a N/S-doped carbon matrix as An Efficient Bifunctional Electrocatalyst for Oxygen Reduction and Evolution Reactions in Zn-Air Battery

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The development of high-performance non-precious bifunctional electrocatalysts for both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) is urgently needed to realize the commercialization of rechargeable metal-air battery. Herein, we report a ZIF-67 derived hybrid Co-based carbon composite bifunctional ORR/OER electrocatalyst exhibiting excellent performance and stability in a custom-built Zn-air battery. The catalyst was formed by pyrolytic carbonization of ZIF-67 followed by mild oxidation and sulfurization to a hybrid composite comprised of multiple active sites including Co-N_4, Co-N/S-C, C-N/S-C, Co_3O_4 and CoS, as well as the surface and edge defects in the carbon matrix, that act concertedly yielding a highly efficient bifunctional ORR/OER catalyst for reversible oxygen electrodes. The catalyst affords remarkably low reversible overpotentials and stability not only in a 3-electrode system, but also in a custom-constructed Zn-air battery, exhibiting competitive performance against benchmark bifunctional ORR/OER electrocatalysts reported to-date and thus placing it among the best non-precious metal catalysts for reversible oxygen reactions.

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Electrochemical Ammonia Synthesis by Molybdenum-Decorated Rhodium Catalysts

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Ammonia is one of the important chemicals for the global economy, and generally used for the production of fertilizers, refrigerants and other chemical feedstock. Recently, ammonia is also being considered as an energy carrier due to its' high density of hydrogen and carbon-free nature.[1] Haber-Bosch process which is the main route for ammonia synthesis, requires huge energy consumption, high purity of hydrogen and harsh reaction conditions. To overcome such limitations, electrochemical method for ammonia synthesis at ambient conditions has been received much attention.[2] In this study, a molybdenum decorated rhodium electrode (Rh_{Mo}/C) is fabricated using an electrodeposition technique. The Rh_{Mo}/C produces a higher yield of ammonia and shows a higher faradaic efficiency comparing with a commercial Rh/C electrode in alkaline media. The electrochemical ammonia synthesis tests have been also conducted in various reaction conditions such as electrolytes and operating potentials. This study reveals the relationship between the reaction condition and the selectivity of ammonia synthesis.

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Operando Observation of a Highly Reversible Nonporous Sodium Metal Anode with Shiny-Smooth Surface

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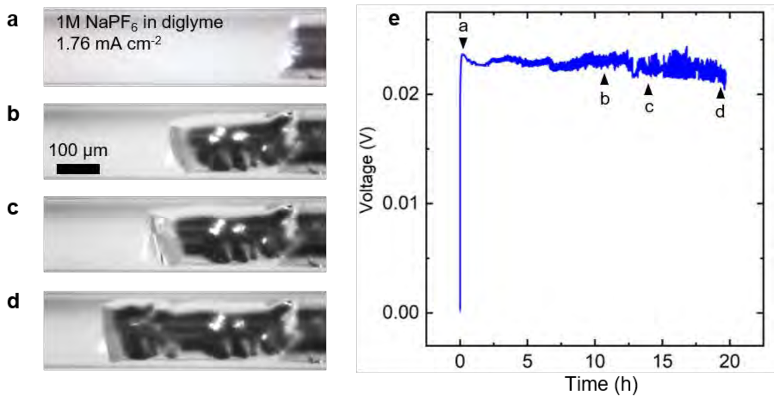
While alkali metal anodes are considered as the promising alternatives to the ion-hosting materials due to the high energy densities, the nonuniform deposition (dendritic growth) that can lead to internal shorts remains a major obstacle of their practical applications (1,2). Here, according to the *operando* observation in our special capillary cells, we report a shiny-smooth nonporous sodium metal anode that can be cycled reversibly even at high areal capacities, without the formation of any whiskers, mosses, gas bubbles or disconnected metal particles observed in existing studies (3,4). The plating process follows the lateral surface-growing mechanism, which transforms into tip-growing branch-like dendrites at a critical time when applying over-limiting currents (5). The observation reveals the possibility that the solid electrolyte interphases (SEIs) are absent, which is supported by the elemental depth profile analysis. As a result, a reversable high capacity sodium metal anode is achieved in coin cells within a critical penetration-related current density (6 mA cm^{-2}). Our study demonstrates the possibility of plating shiny-smooth reactive alkali metal in liquid electrolytes and provides a reliable option applicable for the next-generation alkali metal batteries.



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Nanostructured FeN4-C Electrocatalysts for Energy Conversion in Bioelectrochemical Systems

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Bioelectrochemical systems (BESs) are an efficient and flexible platform for energy recovery and wastewater treatment. However, the slow kinetics of the oxygen reduction is one of the main factors that leads to the use of expensive catalysts, such as platinum, limiting the overall performance output of BESs [1,2]. Platinum group metal-free catalysts supported on nanostructured carbon allowed to achieve oxygen reduction reaction (ORR) rate comparable to commercial Pt based catalysts [2]. ORR active sites efficiency and activity are strongly affected by catalyst structure, morphology and carbon scaffold doping chemistry: nitrogen-doped carbon-based materials exhibit a great ORR catalytic activity [3]. We have previously demonstrated that nitrogen-doped nanostructured carbon is an optimal substrate to support FeN4 macroclycles, due to its high surface area, adjustable electronical and mechanical morphology, and tuneable surface [4]. In this study, iron (II) phthalocyanine (FePc) was anchored on carbon black pearls. To introduce nitrogen functionalities in the carbon structure different strategies have been developed, including pre-treatments based on urea as N source and thermal treatments. The catalysts, labelled as FeN4-C, were characterized by combining the use of electrochemical and spectroscopic techniques to correlate the different morphologies and surface chemistry to electrocatalytic activity towards ORR. Figure 1 shows linear sweep voltammetries of a FeN4-C catalyst in neutral environment, together with a schematic of ORR at a surface of a FeN4-C catalyst.

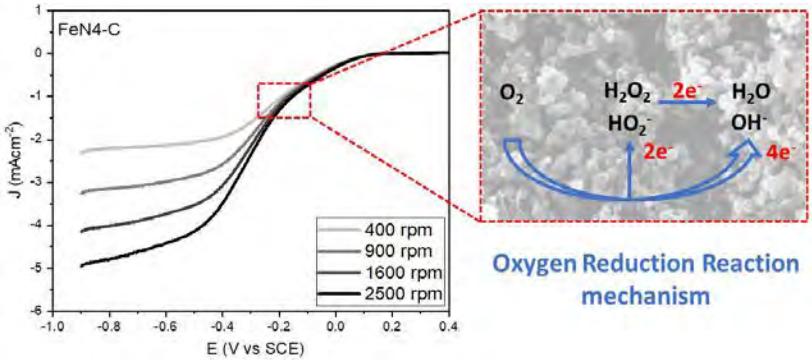

Figure 1. Hydrodinamic linear sweep voltammetries at different electrode rotation rate of FeN4-C catalyst in O_2-saturated 0.1 M phosphate buffer.

As shown in Figure 1, FeN4-N-C onset potential and half wave potential ($E_{1/2}$) were 0.13V and -0.3V vs SCE, respectively, indicating good activity towards ORR. In addition, the application of both Koutecky-Levic theory and rotating ring disk electrode experiments pointed at a charge transfer mechanism close to 4 electrons thus indicating good ORR activity in neutral media. By comparing FeN4-N-C to Pt/C taken as control, the overall performance indicated that FeN4-based electrocatalysts are good candidates to replace platinum for energy conversion in bioelectrochemical systems.

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Copper selenide electrodeposition from a deep eutectic solvent

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Inorganic binary compounds such as Cu-Se and Zn-Se are precursors for the formation of $CuInSe_2$ (CIS), $Cu(InGa)(S,Se)_2$ (CIGS) and $Cu_2ZnSn(S,Se)_4$ (CZTS(Se)), semi-conductor materials selected for the next generation of photovoltaic devices, owing to their near-ideal photo-electrochemical properties. A proper understanding and a good control of the selenium and its binary compounds electrodeposition is thus required to improve the quality of the semi-conductor materials. Deep Eutectic Solvents are nowadays emerging as promising and cheap alternative media for the electrodeposition of metals or compounds that cannot be easily prepared in aqueous or conventional organic solvents.

In the present work, the electrodeposition of copper selenides thin films has been investigated in the choline chloride-urea (ChCl-U) deep eutectic solvent at a gold electrode using cyclic voltammetry. The strategy is focused on previews results [1, 2] in which the electrodeposition of selenium was conducted at various temperatures. At 110 °C, grey (trigonal) selenium was deposited at a potential of -0.4 V (vs. Ag QRE) using SeO_2 as the precursor. At potentials around -0.7 V (vs. Ag QRE), the electrodeposited Se (0) is reduced to Se (-II) and stripped from the surface. This cathodic stripping forms the basis of our strategy to form a copper selenide compound by electrodeposition.

In the presence of dissolved SeO_2/Cu_2O mixtures as precursors at 110°C, the reduction of Se(0) to Se(-II) proceeds at less negative potentials, being coupled with the formation of copper selenide in one step by a proper choice of the deposition potential. The voltammetric responses obtained by varying the deposition potential showed that the electrodeposition of Cu_2Se can be carried out at -0.4 V.

XPS and XRD characterisations point to the formation of Cu_2Se. Photoelectrochemical measurements have been conducted to characterize the semiconductor behavior and the photochemical stability of the electrodeposited material.

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Long-Term Performance Assessment of Commercialized Coating Systems via EIS and SVET

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The performance of conventional solvent-based and newly developed waterborne coating systems was assessed via the electrochemical impedance spectroscopy (EIS) on the surface and Scanning Vibrating Electrode Technique (SVET) at the cut-edge and then benchmarked with natural exposure results [1-2]. It was observed that the developed environmental-friendly coating system has a slightly poorer performance via EIS compared with the conventional coating system in the coil-coating industry. The undercutting corrosion in the waterborne coating was also slightly more noticeable in comparison with the conventional solvent-based system at the cut-edge. The most important outcome of the study, however, was the ability to predict the long-term performance of these coatings by matching the trends obtained via EIS and SVET to the natural exposure results. Correspondingly, the results from the same coating systems after two years of exposure suggest that the conventional system tends to be more corrosion resistant compared to the environmental-friendly coating system. The reasons for different performances have also been discussed based on the inhibition efficiency of corrosion inhibitors doped within the organic coating, and also the effect of substrate chemical composition on corrosion performance of the system.

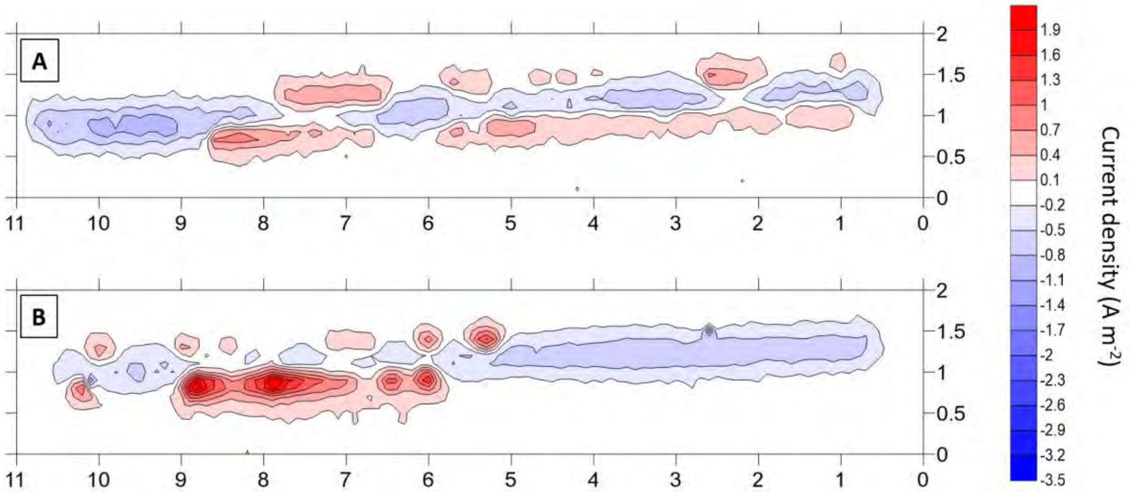

Figure 1 – SVET current density maps: (A) conventional solvent-based coating, and (B) environmental-friendly waterborne coating systems after 12 hours in 5 wt.% NaCl solution

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Ni-Based Alloy Nanostructured Electrodes for Alkaline Electrolyzers

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In recent years, the installed power of renewable energy sources plants has considerably grown increasing [1]. One of the main drawbacks of renewable sources is their unpredictability, consequently they need a storage system that can efficiently manage the produced energy. In this scenario, the electrochemical production of hydrogen could play an important role in the future. However, the electrochemical hydrogen production cost is still too high in respect to other technologies. For this reason, research is focused on improving the electrolyzers performance, through the use of more efficient and less expensive materials, such as transition metal alloys [2].

In water alkaline electrolyzer field, the development of Nickel-based nanostructured electrode is one of the possible ways to improve the water electrolysis efficiency [3]. In particular, through the use of a simple manufacturing method, template electrosynthesis, it is possible to realize high density surface area electrodes. In previous works, Ni nanowires electrodes for water-alkaline electrolysis covered by nanoparticles of IrO_2 as an anode and Pd as a cathode have shown good and stable performance also at room temperature [4-5].

In this work, using the template electrosynthesis for nanostructures fabrication, the attention has been focused on the electrodeposition of Ni-based alloys. Several different alloy electrodes were manufactured starting from different aqueous solution containing various transition metal, such as zinc, cobalt and tungsten. Tuning the elements concentrations in the solutions and the electrodeposition operating conditions, alloys with different compositions have been obtained. Morphological and chemical nanostructured electrodes features will be presented and discussed. Moreover, electrochemical and electrocatalytic test carried out to evaluate the best alloy composition will be shown. Then, long term test conducted at a constant current density in aqueous solution of potassium hydroxide (30% w/w) at room temperature will be also reported.

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Increasing the diameter of the vertically ordered pores in silica thin films produced by electrochemically assisted self-assembly

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The vertical alignment of pores in hexagonal mesoporous silica films can be achieved through the electrochemically assisted self-assembly method (EASA).[1,2] An appropriate negative potential is applied to a solution containing the surfactant and inorganic precursors solubilized in an ethanol/water mix. This results in the generation of hydroxide ions in solution, whereby, the pH swings from acidic to alkaline at the electrode surface. The electric field plays a pivotal role in the self-organization of the cationic surfactant into hemi-micelles and the pH change catalyses the polycondensation of the silica sol.[3,4] Our interest in well-ordered vertically aligned EASA films is the possibility of utilizing them as feasible templates for the electrodeposition of few nm-diameter metal and semiconductor nanowires. Previous works reveal that it is possible to electrodeposit nanowires into porous silica templates[5,6]. However, the stability of very small nanowires is poor in pore diameters below 2 nm.[7] Here we demonstrate that systematic increases in the pore diameter ($>$ 2 nm) are achievable by EASA, utilising larger surfactants formed by extending the single straight alkyl chain. Additionally, replacing the methyl substituent of an ammonium polar head group is another route to pore diameter expansion.

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Glycerol electro-oxidation in acidic and alkaline media at different temperatures on polycrystalline and single crystals Pt electrodes

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The demand for greener sources of energy resulted in a higher production of biodiesel, and consequently glycerol, since it is a co-product of the biodiesel synthesis that has surpassed the industrial demand. Due to this issue, many research groups have been investigating alternatives to use this excess[1]. In this context, the electro-oxidation of glycerol (EOG) is an interesting option towards the chemical valorization of this compound, generating value-added products and high purity H_2 in electrolysers[2].

The EOG has been studied in Pt in both acidic and alkaline media[3-5], however, at least to our knowledge, there is any study about the effect of the temperature in the activity and selectivity of the reaction. Thus, herein we study the EOG on Pt polycrystalline (Pt_p) and Pt single crystals electrodes of the main crystallographic orientations: Pt(111), Pt(100) and Pt(110) at 5 °C and 35 °C. *In situ* FTIR and electrolysis coupled to HPLC will be performed to understand the electrochemical results in terms of products and/or intermediates that are formed during the EOG.

Figure 1 shows results obtained in alkaline media. Interestingly, this preliminary results suggests that the temperature acts increasing the rate of all the parallel processes occurring at each electrode, generating changes in the current densities, but not changing the I-V response shape. For Pt(110), the increase in the current density was approximately fourfold, threefold for Pt(100) and twofold for Pt(111), i.e., as more open the surface is, higher the temperature activation. It is well-known that as more open the surface is, more prone to poisoning it becomes, then we suggest that the increase of the temperature help to detach strongly adsorbed adsorbates, contributing more to the enhancement of the currents of the more poisoned electrodes.

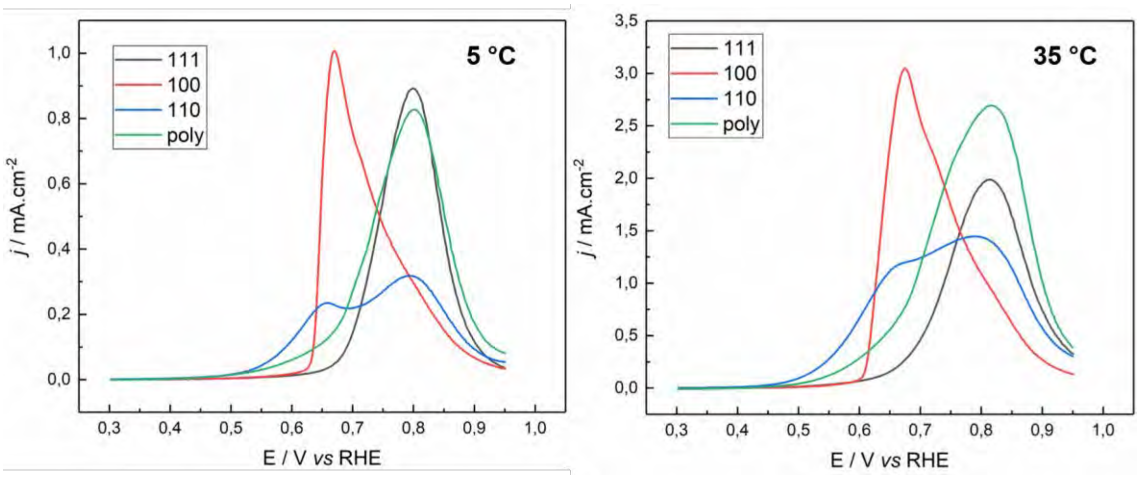

Figure 1 – 10th positive scan of the EOG in 0.1 M NaOH + 0.1 M GlOH for all the electrodes at 10 mV/s.

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Electrochemically Addressable Nanofluidic Devices based on the Integration of Electroactive Polymers into Solid-State Nanochannels

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Solid-state nanochannels have attracted the interest of the scientific community due to its controlled mass transport properties. Particularly, the ionic transport through these nanometer-sized channels is strongly dependent on the geometry and surface charge of the channel walls. The modulation of the surface charge density allows modifying the permselectivity and consequently the conductance of solid-state nanochannels which has huge implications in fields such as electronic, biosensing, and filtration.[1] Considering this fact, there has been an increasing interest in the development of nanofluidic devices with the capability of controlling the surface charge density, and therefore the ionic transport, by experimentally controllable stimuli, such as temperature, pH, electrical potential, light, or the presence of an analyte in solution.[2] However, most of these conditions are difficult to control in confined spaces. In this context, the electrochemical stimuli-based strategy is especially promising since it enables to regulate the ionic currents by an external and easy to control experimental input. In this sense, the integration of electroactive polymers into solid-state nanochannels offers a suitable option to accomplish this aim. Thus, the use of redox-active bistable molecules that can be switched between different oxidation states by addressing an external electrical potential would allow an easy modulation of the surface charge on the nanochannel walls and, consequently, to govern the nanofluidic readout with a fast and highly efficient response.

Within this framework, we present our recent results concerning the integration of electroactive polymers into solid-state nanochannels for developing electrochemically-addressable nanofluidic devices.[3–6] We show how the combination of electroactive polymers and solid-state nanochannels can lead to a myriad of new designs of switchable nanofluidic devices with potential applications in different fields such as biosensing, drug delivery, or filtration.

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Integration of Conducting Polymers and Metal Organic Frameworks for boosting Oxygen Reduction Reaction performance: a Nanoarchitectonics Approach

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The term “Nanoarchitectonics” involves the integration of molecular building blocks into well-defined organized assemblies via a variety of approaches, where the intimate connection between the materials gives origin to improved functionalities or even creates new ones. Among the vast spectrum of available strategies, Layer-by-Layer (LbL) and electropolymerization are two of the most employed approaches for creating functional materials for electrochemical applications. While LbL allows for an accurate manipulation of film architecture and the incorporation of numerous building blocks; electropolymerization offers a precise control of film thickness, morphology, and composition, thus allowing the inclusion of desired moieties for further surface functionalization.

On the other hand, Oxygen Reduction Reaction (ORR) is an essential electrochemical process in many energy conversion devices, taking particular relevance in facing the increasing global demand for clean energy sources and vectors. Desirable features for ORR-based catalysts are operability under environmentally friendly conditions, biocompatible electrolytes, and the reduction of metal loadings. [1]

Having in mind the above discussion, we hereby present examples of the integration of Conducting Polymers (CPs) and Metal Organic Frameworks (MOFs) through different approaches in order to construct assemblies featuring improved ORR performance. In this way, the O_2 adsorption ability and high porosity of the Zn-based MOF ZIF-8, and the electroactivity of polyaniline-like CPs are effectively brought together by making use of LbL assembly and electropolymerization techniques.

In the first example, the LbL strategy is employed in order to perform the sequential assembly of colloidal suspensions of the polyaniline/polystyrene sulfonate complex (Pani-PSS) and polyallylamine hydrochloride-coated ZIF-8 nanocrystals (PAH-ZIF-8). The LbL-assembled films are found to be electrically connected and feature promising increases in the ORR current in neutral pH aqueous environments.[2]

On the other hand, we introduce the use of electropolymerization as synthetic strategy for producing electroactive films featuring $-NH_2$ moieties. Then, a MOF coating is integrated by induced growth on the amino pending moieties from the methanolic precursor solutions. This strategy generated a composite film with improved ORR performance due to the effective combination of the electroactivity of the CP and the MOF capacity of acting as an oxygen reservoir.[3] Moreover, this approach also allows the incorporation of metallic nanoparticles (NPs) in order to improve the overall electrocatalytic performance of the nanocomposites. In this way, the in-situ reduction of the Pt NPs precursor on the CP not only keeps the electroactivity of the conducting matrix but also improves its electrocatalytic efficiency. Subsequent deposition of the MOF coating further increases the ORR performance, by adding the O_2 preconcentrating effect. [1]

Finally, nanoarchitectonics can be seen as a toolkit from which different strategies can be taken in order to construct complex interfacial architectures with improved ORR features arising from the combination of the different building blocks.

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Selective Recognition by Nanoparticle-Imprinted Matrices

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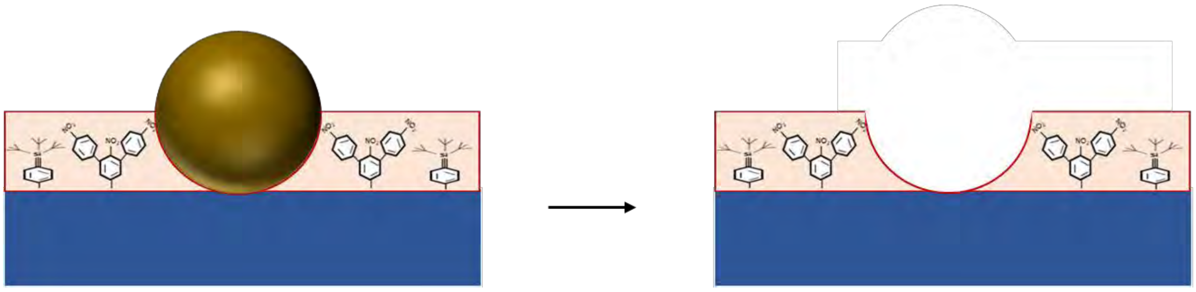
Nanoparticles (NPs), being the suitable candidates for various commercial and domestic applications due to their unique physical and chemical properties are now widely used in medical, automotive and ecological arenas. A major drawback is their uncontrolled release to the ecosystem paired by inadequate detection techniques selective to size, shape and chemical nature of core material as well as shell. Those parameters decisively determine the toxicity of NPs. This calls for facile tools to detect NPs based on the above factors. We work towards the development of simple, inexpensive and miniature sensing layers capable to selectively enrich NPs on surfaces. The work follows the idea of nanoparticle-imprinted matrices (NAIM), with some analogy to the well-known molecularly imprinted polymers (MIP). Electrochemistry is used to deposit a thin film, which is homogeneous, highly stable and thick enough to provide size-selective recognition of nanoparticles [1].

Electroreduction of 4-((triisopropylsilyl)ethynyl) benzene diazonium salt followed by the electroreduction of 4-nitrobenzene diazonium salt yields a matrix, which is 7-9 nm thick on an indium tin oxide (ITO) coated glass substrate. The initial layer is formed from a diazonium salt with a bulky substituent to induce steric hindrance, thereby preventing inhomogeneous, highly rough film formation [2]. The films are characterized by scanning force microscopy, photoelectron spectroscopy and infrared reflection absorption spectroscopy. Such a film entraps the template NPs on the substrate and forms a matrix. Later, the template NPs are removed by chemical etching which forms a cavity complementary to the template NPs used, forming a NAIM. This NAIM is then exposed to analyte NPs, expected to selectively recognize them based on their shape, size and shell.



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Structural modifications of model lipid rafts exposed to selected statins – Langmuir and electrochemistry studies.

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Statins are a group of drugs that are responsible for lowering cholesterol levels by inhibiting the reductase 3-hydroxy-3-methyl-glutaryl-enzyme A (HMG-CoA). They are widely used to prevent cardiovascular diseases [1,2] and can be divided according to their origin into natural and synthetic ones [3]. These drugs interact not only with proteins but also have an effect on the organization and surface properties of lipid membranes.

Preparation of model biological membranes at the air-water interface by means of Langmuir technique allowed us to assess the influence of selected statins on the lipid packing in the membranes and the fluidity of the layers. The lipid systems used consisted of phosphocholines (DOPC), sphingomyelin and cholesterol which are the main components of lipid rafts. The effect of the three selected statins (pravastatin, fluvastatin and cerivastatin) on muliticomponent monolayers was first investigated. The effect of statins strongly depends on the properties of the drug itself, since molecular differences between statins' structures may lead to the changes in functions that affect cellular processes [1]. It has been shown that pravastatin changes the surface properties of the layers only slightly. More lipophilic fluvastatin penetrated the model membranes much easier while cerivastatin had a fluidizing effect, but only slightly changed the packing of the polar headgroups in the lipid monolayer. The second stage of the research involves the transfer of layers from the air-water interface to a solid substrate by the Langmuir- Blodgett/Langmuir-Shaefer method. The effect of selected statins on multicomponent layers forming lipid rafts (DOPC:SM:Chol), was studied using electrochemical impedance spectroscopy. Biological membranes by their structure act as capacitors, hence impedance experiments allowed us to assess changes in their capacity and barrier properties following exposure to statins.

Our experiments showed the specific nature of the interaction of cerivastatin with model membranes and its negative effects upon the membrane organization which may explain why this drug was withdrawn from the market. Based on the performed measurements it is possible to understand better why these drugs, so effective in decreasing levels of cholesterol, can also lead to unwanted disorders of the nervous system and myopathy, threatening the proper functioning of our body.

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Electrochemistry for Climate Change:

CO_2 Capture by An Electrochemically Mediated Amine Regeneration Process

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Abstract

Global warming resulting from the emission of greenhouse gases, especially carbon dioxide (CO_2), has become a major concern in recent years. The global concentration of CO_2 in the atmosphere is increasing rapidly; in May 2019, atmospheric CO_2 reached 415 ppm, which is the highest level in more than 800,000 years. This prompted research activity to develop various approaches that could effectively mitigate emissions by capturing CO_2, especially from large-point sources such as post-combustion flue gas. It is believed that electrochemistry, a key part of the 2019 Nobel Prize in Chemistry, is a powerful, emergent tool for the design of different approaches to directly or indirectly assist in achieving the goals in the action plan by effectively mitigating CO_2 emissions. Electrochemistry will offer a unique advantage in the future, when the electrical energy is mostly generated by renewables. The carbon footprint and the cost of the electrochemical processes would be minimized, making them an attractive solution for addressing climate change. In this context, different approaches based on electrochemical processes have been proposed to drive CO_2 capture and release. We recently demonstrated an electrochemically-mediated amine regeneration (EMAR) process as a low-energy, efficient, and potentially scalable method of capturing CO_2 from flue gas. The EMAR process scheme is similar to that of the amine-based thermal approach, but the high-temperature scrubbing stage is replaced with a two-compartment electrochemical cell that operates at a moderate temperature. During the EMAR process, a CO_2-rich amine stream from the absorber is introduced to the anode compartment of an electrochemical cell, in which copper ions are electrochemically generated from a copper plate anode (i.e., $Cu^0 \rightarrow Cu^{2+} + 2e^-$) to drive the dissociation of amine-CO_2 toward CO_2 desorption (i.e., Cu^{2+} + n amine-$CO_2 \rightarrow$ Cu(amine)$_n^{2+}$ + n CO_2). Once the gas is flashed off through a flash tank located after the anode compartment, the CO_2-lean stream is regenerated via the electrochemical plating of copper on the cathode from the copper-amine complex (i.e., Cu(amine)$_n^{2+} + 2e^- \rightarrow Cu^0$ + n amine). Therefore, CO_2 capture and release can be achieved by chemical absorption followed by electrochemical regeneration of the absorbent through the EMAR process.

To determine the best combination of metals and amines for the EMAR process, a systematic analysis of several transition metals together with monoamines, diamines, and polyamines was performed. A combination of copper as the metal and a mixture of ethylenediamine (EDA) and aminoethylethanolamine (AEEA) as the amine absorbent was found to be the most effective chemistry for the EMAR cycle, mainly due to the high stability constant of the copper complexation with the amines, a suitable reduction potential of the complex, high CO_2 capacity, good reversibility, high electrochemical performance, and low cost. Based on this chemistry, we scaled up the EMAR process to a level at which continuous CO_2 capture and desorption from flue gas was achieved over longer than 100 hours. We also showed that electrical energy can be efficiently translated to CO_2 desorption, with an electron utilization (i.e., moles of CO_2 desorbed per mole of electrons transferred) of ~0.8 over more than 50 cycles. To date, the EMAR system is the most advanced and scaled-up system in terms of gas desorption rate and efficiency among all the electrochemical processes developed for CO_2 capture from flue gas streams.

Keywords: climate change; CO_2 capture; flue gas; electrochemical process; EMAR; scaled-up system; long-term experiment

Gas Diffusion Electrode Setups:
A New Testing Platform For Electrocatalyst Evaluation

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Accurate testing platform and efficient electrochemical characterization method play a key role in development of electrocatalysts in fuel cells and CO_2 electrolyzers. Currently, two approaches are well-established: rotating disk electrode (RDE) or H-type half-cell setups with liquid electrolyte as well as single-cell tests with membrane electrode assemblies (MEAs) [1]. The former has the disadvantage of mass transport limitations, which significantly limits the “accessible reaction rate” that can be analyzed, and the latter requires specialized equipment and large quantities of catalyst, making them less ideal for early-stage development [2]. Recently we introduced a gas diffusion electrode (GDE) setup to overcome these limitations [3]. This setup allows the investigation of the electrocatalysts under realistic conditions so it can be considerd as a link to bridge fundamental and applied investigations. In the presented work, we discuss the application of GDEs for investigating the stability of high surface area fuel cell catalysts under realistic reaction conditions in acidic [4] and alkaline media. In addition, we show the identical location transmission electron microscopy (IL-TEM) images which were taken before and after the accelerated degradation test (ADT). Moreover, we implemented the characterization of the catalysts by small-angle X-ray scattering (SAXS), which establishes the particle size distribution in the catalyst layer. In contrast to IL-TEM, SAXS is an integral method which probes changes in the entire catalyst layer before and after performing the ADT [5]. Furthermore, we demonstrate how the carbon dioxide reduction reaction (CO_2RR) can be studied with simple minor changes to the setup [6].

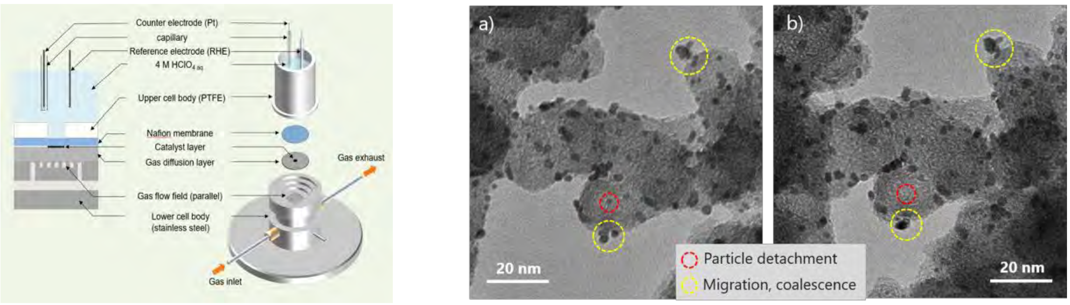

Fig.1 The sketch of the GDE cell (left) and IL-TEM micrographs of a commercial 20 wt. % Pt/C catalyst (HiSPEC 3000) before and after load-cycle ADT treatment for 1200 cycles at 60 °C (right).

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Acid mine drainage treatment by means of bioelectrochemical technology

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Acid mine drainage (AMD) is an environmental problem mainly associated with the mining activity. AMDs are characterized by high concentrations of a wide variety of metals, high concentration of sulphates and low pH.

This work has studied the sequential cathodic removal of four metals (Cu^{2+} 500ppm, Fe^{3+} 500ppm, Ni^{2+} 50ppm and Sn^{2+} 50ppm) from a simulated AMD by using a bioelectrochemical system, first working as a microbial fuel cell (MFC) and then as microbial electrolysis cell (MEC).

Operating as MFC, Fe^{3+} was reduced to Fe^{2+} and Cu was deposited onto the cathode. All the Cu was recovered after 4 days and generating about 0.12 mA/cm2. When operating as MEC the Fe^{2+}, Ni^{2+} and Sn^{2+} were simultaneously removed by fixing the cathode potential at -0.7 V vs Ag/AgCl, getting a current density of 1.75 mA/cm2. This stage recovered all the Sn, 60% of the Fe and 75% of the Ni in 3 days.

Financial support from projects EQC2018-004240-P, SBPLY/19/180501/000254 "Rehabilitación de entornos abandonados de minería metálica y recuperación de recursos mediante tecnologías bio-electroquímicas" and from the FPI grant to L.F. León through the reference BES-2017-081718 from the Spanish Ministry of Economy, Industry and Competitiveness are gratefully acknowledged..

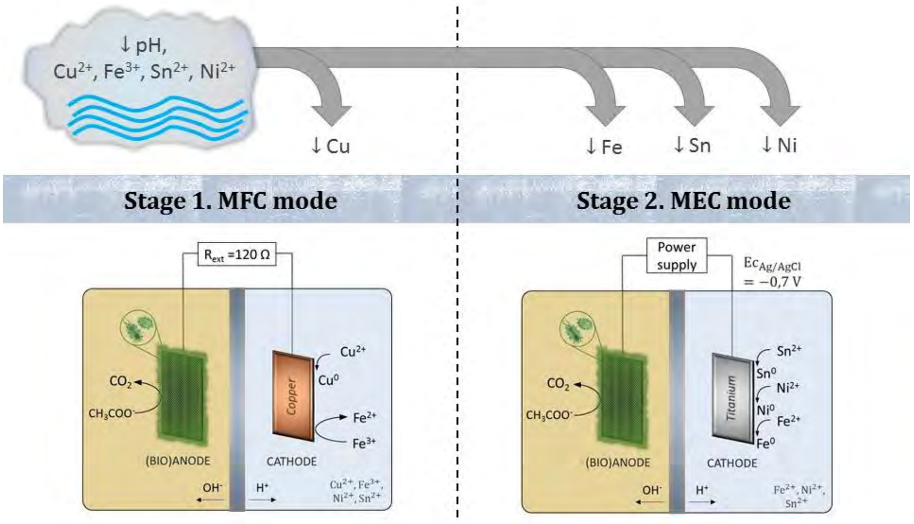

Figure 1. Scheme of the AMD treatment and sequential metal recovery process.

Enhancement of the cathodic dechlorination of 2,4-DCP in bioelectrochemical systems

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The use of organochlorinated pesticides and herbicides to enhance the production of crops may produce soil and groundwater pollution. 2,4-dichlorophenol (2,4-DCP) is one of these compounds, mainly used as precursor of 2,4-dichlorophenoxyacetic acid (2,4-D), a commercial herbicide. In this work, a novel treatment of 2,4-DCP by using bioelectrochemical systems (BESs) was studied.

This work studies the influence of the cathode pH and energy input on the electroreductive hydrodechlorination of 2,4-dichlorophenol (24DCP) in an abiotic cathode. When operating as BES as Microbial Fuel Cell (MFC), the results showed that more acid cathode pH enhances the electrocatalytic hydrodechlorination (ECH), reaching a total dechlorination after 72 h. Also, ECH was further enhanced by operating under Microbial Electrolysis Cell (MEC) mode, where the cathode was poised towards more negative potentials and higher current densities were achieved. The dechlorination was directly linked to the toxicity reduction and biodegradability increment, allowing to a subsequent biological treatment of the effluent generated which reduces the treatment cost of this kind of recalcitrant pollutants

Financial support from projects EQC2018-004240-P, CTM2016-76197-R (AEI/FEDER, UE) from the Spanish Ministry of Economy, Industry and Competitiveness and European Union and from the FPI grant to L.F. León through the reference BES-2017-081718 from the Spanish Ministry of Economy, Industry and Competitiveness are gratefully acknowledged.
These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

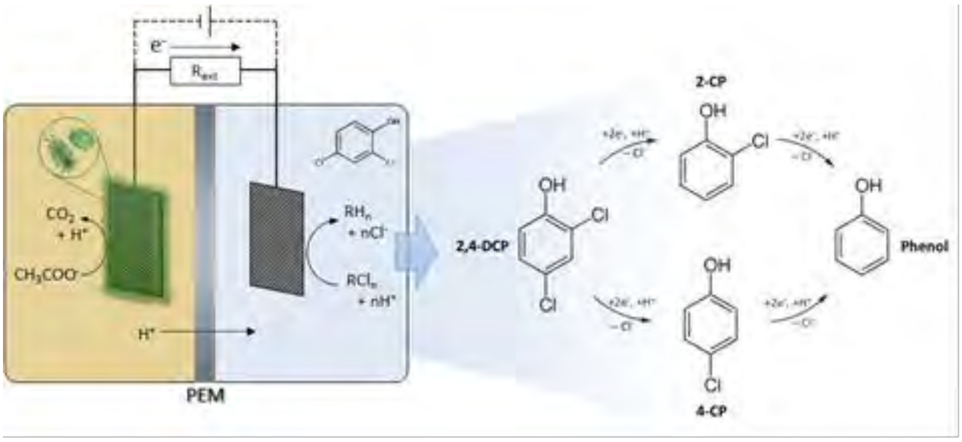

Figure 1. Scheme of the bio-assisted electroreductive dechlorination process.

Electrochemical P53 Gene Detection of DNA by Formation of Efficient Electron Transfer Pathways through Adsorbing Gold Nanoparticles to DNA Modified Electrodes

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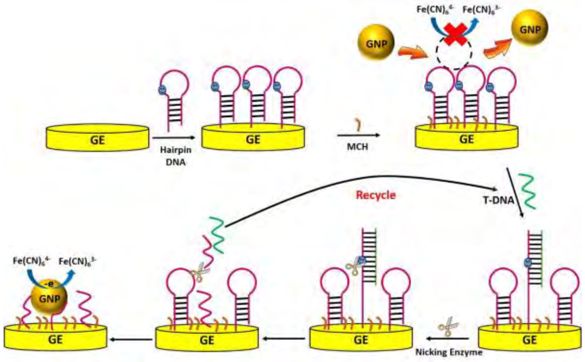
Abstract

P53 gene plays a vital role in regulating cellular processes and its accurate quantification is of great significance to the early screening of cancers.[1, 2] Here, we proposed a simple and label-free electrochemical DNA biosensor based on the gold nanoparticles (GNPs) mediated electron transfer (ET) across different DNA monolayers modified on (gold electrode) GE surface and we also introduce nicking endonuclease-assisted signal amplification (NESA) into the bio-sensing system. Additionally, hairpin DNA (HPDNA) was first employed in our work for better understanding of the how the different status of DNA strands monolayers on electrode surface affect GNPs mediated ET process. The working principle of p53 gene biosensor is illustrated in Scheme 1. Specifically, compared to single-strand DNA (ssDNA), the HPDNA is a relatively rigid structure[3] which can prevent the adsorption of GNPs onto the GE surface, such blocking events cannot introduce enhanced ET between electrode and redox species. However, the nicking endonuclease could bind to and nick the recognition site embedded into the loop portion of the HP after its hybridization with p53 gene. After nicking, the HP would be cleaved into two pieces. The resulting ssDNA on the GE could adsorb GNPs because of the electrostatic interaction between gold and nitrogen-containing bases.[4] Thus, the negative electrochemical species $[Fe(CN)_6]^{3-/4-}$ can transfer electrons to electrode through adsorbed GNPs. The charge-transfer resistance (R_{ct}) will dramatically decrease with the increase of cleavage of HPs. Consequently, the change of R_{ct} is directly proportional to the hybridization of p53 gene. Additionally, with the assistant of nicking endonuclease, p53 gene can be reused and hugely lower the detection limit. The proposed biosensor toward p53 DNA achieves a detection limit of 0.0835 fM with a linear calibration range of 0.1 fM ~ 1 fM. Moreover, the prepared biosensor also exhibited excellent sequence selectivity and reproducibility, demonstrating this strategy was promising for enormous potential application in clinical diagnostics and biomedical research.



Scheme 1. Schematic Diagram of the NESA coupled GNPs electrochemical biosensor for the detection of p53 gene.

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Development of a portable electroanalytical method using nickel modified screen-printed carbon electrode for ethinylestradiol determination in organic fertilizers

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Urine and struvite are promising organic fertilizers that can replace conventional fertilizers[1]. However, these fertilizers may contain some emerging organic contaminants, such as hormone. One of the most common hormones is the ethinylestradiol, which can be found in aquatic environments and can cause several changes in living organisms, including deregulation of fish endocrine glands, which can promote the feminization of some species[2]. Thus, the present work developed a fast, sensitive, and portable method for determining ethinylestradiol in urine and struvite, using square wave voltammetry (SWV) and screen-printed carbon electrodes modified with nickel film (SPCE-Ni).

SPCE modification was performed by cyclic voltammetry (CV) and the variables of interest (number of cycles (NC), scan rate (SR) and nickel ion concentration ($[Ni^{2+}]$)) were optimized using factorial design 2^3 and central compound design (CCD). The application of factorial design demonstrated that the variables NC and $[Ni^{2+}]$ are significant. Therefore, these variables were submitted to CCD planning (SR was set at 5 V s^{-1}). Fig. 1 shows the results obtained by CCD, the optimal values chosen for NC and $[Ni^{2+}]$ were 1000 and 9.4 mmol L^{-1}, respectively.

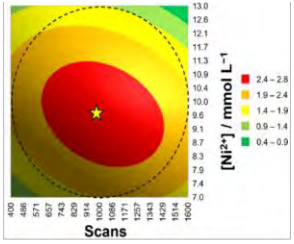

Fig.1. Level curve obtained for the optimization of the variables: number of cycles and concentration of nickel.

The SPCE-Ni and SPCE were characterized by Raman spectroscopy, to identify the modification performed on their surfaces. Fig. 2 shows Raman peaks at 304, 450, 473, 490, 526, and 552 cm^{-1}, what can be attributed to the presence of $Ni(OH)_2$ and NiOOH[3,4]. The results demonstrate the possible presence of different nickel compounds on the surface of the SPCE, especially NiOOH which has electrocatalytic activity in the oxidation of organic molecules[5]. The pH effect on the voltammetric response of ethinylestradiol was evaluated by CV, in the pH range of 3.0 to 10.0, using KCl and BR buffers in the presence of 10.0 µmol L^{-1} of the analyte. The results demonstrate that 0.1 mol L^{-1} BR buffer solution (pH 8.0) was the best support electrolyte. The optimization of the SWV operational parameters was also performed by factorial design (2^3) and CCD. The optimal values found were: 10 mV (step potential), 40 mV (modulation amplitude) and 20 Hz (frequency).

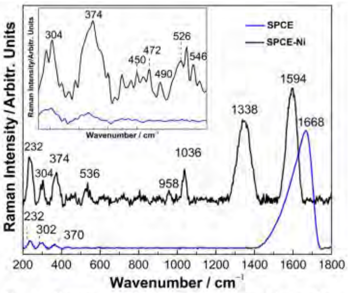

Fig. 2. Raman spectrum of the screen-printed carbon electrode surface (—) SPCE and (—) SPCE-Ni.

The analytical curve was constructed in a linear range of 0.23 to 30.0 µmol L^{-1} (Fig 3). The method presented a limit of detection (LOD) and quantification of 0.067 and 0.228 µmol L^{-1}, respectively, and R^2 of 0.996. The determination of ethinylestradiol in struvite and urine samples indicated that the concentration of the hormone is below of LOD in both. The recovery tests in different matrices showed values between 93.9 and 107.5%, demonstrating that there is no matrix effect. Based on all of these results, the developed procedure can be considered a viable and sustainable alternative to promote green chemistry in the determination of the ethinylestradiol in urine and struvite.

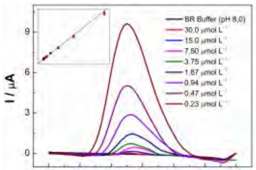

Fig. 3. Square wave voltammograms for the addition of eight solutions of ethinylestradiol (0.23 to 30.0 µmol L^{-1}) in 0.1 mol L^{-1} BR buffer (pH 8.0).

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Electric double-layer structure and adsorption of halides on Au (111) electrode in organic solvent - SEIRAS, XPS and EIS

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Specific adsorption of ions on the electrode surface has a significant impact on the electric double layer (EDL) structure and the kinetics of electrode processes[1]. This has a substantial effect on many disciplines, such as corrosion, galvanic deposition, electrosynthesis, and electrocatalysis[2]. The ion adsorption at aqueous solution interfaces[3] on various metals has been examined intensively, but much fewer studies from non-aqueous solvents have been conducted[4]. Such studies are important because the metal-solvent [5] and ion-solvent interaction energy [6] depend on the chemical nature of the solvent.

In this study, three organic solvents (propylene carbonate (PC), diglyme (DG), and dimethyl sulfoxide (DMSO)) were investigated for the adsorption of iodide and bromide ions on Au(111) single crystal electrode. This analysis was conducted by using differential capacity measurements, cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), surface-enhanced infrared spectroscopy (SEIRAS), and X-ray photoelectron spectroscopy (XPS) techniques.

During SEIRAS measurements, a bipolar band is observed at around 1800 cm^{-1} which correlates to the C-O-vibration of PC as reported on silver electrodes from SERS measurements[7]. Its intensity enhances with going to negative potentials with shifting to lower wavenumbers because of increasing field and highly orientation of PC molecules. While the presence of iodide in the electrolyte results in the shift in the pzc in the negative direction, which leads to stronger alignment of PC molecules in the direction of positive potentials. Anion adsorption charge in DMSO is approximately half the charge in propylene carbonate. Quantification of the adsorbed iodide amount from XPS spectra confirms the calculated adsorption charge from the CVs. The magnitude of anion adsorption on Au(111) electrode increases in the series of halides $I^- > Br^-$ due to better solvation [8] and in the solvent order PC > DG > DMSO.

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New insights into the mechanism of coreactant electrogenerated chemiluminescence facilitating enhanced bioanalytical performance

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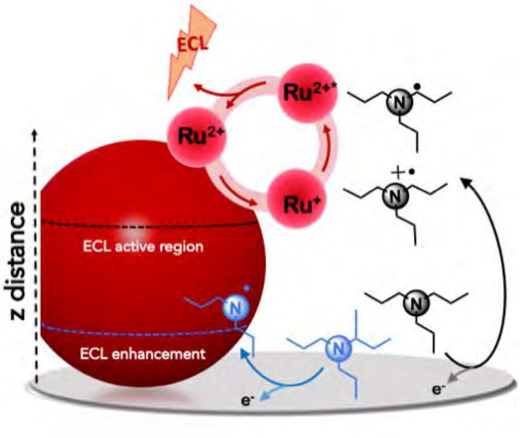
Electrochemiluminescence (ECL) is a leading technique in bioanalysis.[1] Since the excited species are produced with an electrochemical stimulus rather than with a light excitation source, ECL displays improved signal-to-noise ratio compared to photoluminescence, with minimized effects due to light scattering and luminescence background. The most challenging breakthrough in the development of analytical electrochemiluminescence (ECL) applications was reported from Bard and co workers that presented for the first time the generation of ECL with a coreactant.[1] This finding opened the application of ECL to large literature and transformed ECL from an academic curiosity to a real application and industrial success. In this context, the only real used materials for the ECL analytical and commercial application are tripropylamine (TPrA) as sacrificial "oxidative-reductant" coreactant and Ruthenium(II)-tris(2,2'-bipyridine) ($[Ru(bpy)_3]^{2+}$) as emitting species. In this case the mechanism for the ECL generation was proposed by Bard and still nowadays the only one accepted.[2],[3]

Here we show an additional, and very efficient, mechanism pathway for the generation of ECL by using TPrA as coreactant. Thanks to the combination between ECL and microscopy we experimentally prove the alternative mechanism with the standard $[Ru(bpy)_3]^{2+}$/TPrA system.[3],[4] These mechanistic findings allow us to propose alternative amines as coreactant enhancing the ECL signal of more than one order of magnitude.

The reported results, besides contributing to a better understanding of the mechanisms operating in the chemiluminescence generation, also pave the way for the development of very highly efficient ECL coreactants for ultrasensitive bioanalysis.[5]



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Regulating Li-Ion Migration in Solid-State Electrolytes for Li Metal Anodes

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Lithium (Li) metal batteries are strongly considered one of the most promising candidates for next-generation rechargeable batteries due to their high theoretical specific capacity and low reduction potential. However, Li metal anodes are suffering from limited cycle life, low cycling efficiency, and severe safety concerns resulting from sharp Li dendrites and electrolyte degradation.

The uncontrollable Li dendrite growth caused by the uneven distribution of Li ions is an extremely complicated issue coupled with the transport of anions, cations and electrons, as well as the chemical and electrochemical reactions at the anode-electrolyte interphase. In terms of the ion migration, space-charge theory indicates that the electrolyte is divided into a quasi-neutral region and a space-charge region. The quasi-neutral region approaches the cathode side, at which the ion transfer is governed by diffusion. In contrast, when ions travel close to the anode side, the ion transport is mainly driven by the electric field, leaving a space-charge region that accounts for ramified Li metal growth. Consequently, it is rewarding to design electrolytes that can regulate the ion distribution (including both Li cations and the counter anions) to inhibit Li dendrite growths.

Immobilizing anion has been theoretically proved to influence cation distribution, where a portion of immobilized anions (even as small as 10%) contribute to stable Li electrodeposition. Here, we develop an anion-immobilized solid-state composite electrolyte for Li metal anodes. Garnet-type $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) ceramic particles are well dispersed in a polymer matrix to synthesize a polyethylene oxide (PEO)–lithium bis(trifluoromethylsulphonyl)imide (LiTFSI)–LLZTO (PLL) solid electrolyte. In contrast to routine electrolytes with mobile anions, the PLL solid electrolyte contributes to effective immobilization of anions for uniform ion distribution and dendrite-free Li deposition. Chemical and mechanical interactions between ceramic particles and the polymer matrix result in reduced PEO crystallinity and pinned TFSI−anions, enabling relatively fast Li^+ conduction. We further demonstrate the application of this flexible membrane in all–solid-state $LiFePO_4$ (LFP) || Li and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM) || Li batteries.

Moreover, ion migration in batteries can be analogized to the fluid transportation in packed towers in the field of chemical industry. Redistributors are used to intensify the heat and mass transfer processes in a packed tower. Solid-state electrolyte LLZTO, with abundant 3D ion conduction channels, can act as a redistributor to regulate Li-ion distribution. We propose a concept of ion redistributors to eliminate dendrites by redistributing Li ions with LLZTO coated polypropylene (PP) separators in Li metal batteries. The standard deviation of ion concentration beneath the LLZTO composite separator is 13 times less than that beneath the routine PP separator. This approach enables a high specific capacity for $LiFePO_4$|| Li pouch cells and prolonged cycle life span of 800 hours for Li || Li pouch cells. This strategy is facile and efficient in regulating Li-ion deposition by separator modifications and is a universal method to protect alkali metal anodes in rechargeable batteries.

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Oxygen reduction reaction on rough massive gold electrodes – Surface roughness as adjusting screw

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Surface roughness is a parameter, which is scarcely addressed in current publications, despite the fact, that the surface structure can strongly affect the product distribution of an electrochemical reaction. In this work, we show the change in ORR product distribution in Li^+ and Ca^{2+} containing dimethyl sulfoxide (DMSO) on gold. In case of Ca^{2+} containing DMSO we furthermore investigate the possibility of using the surface roughness as tool to get additional insights into the reaction kinetics. This investigation is supported by methods like Differential electrochemical mass spectrometry (DEMS) and rotating ring disk electrode (RRDE) generator collector experiments. It is already known that on gold electrodes in Li^+ containing DMSO soluble superoxide is formed prior to insoluble Li_2O_2 during ORR.[1-3] We found, that in case of Li^+ containing DMSO on gold electrodes, the amount of generated O_2^- is constant for all roughness factors (f_R) during a cycle, while the amount of insoluble Li_2O_2 increases linearly with f_R corresponding to a slope of approximately $660\frac{\mu C}{cm^2}$, finally leading to a complete deactivation of the electrode. In case of Ca^{2+} containing DMSO a continuous generation of soluble superoxide, even at CaO_2-saturated electrodes is already known ond gold electrodes.[4, 5] We furthermore found diffusion limited formation of soluble CaO_2 on rough Au electrodes. From the change in half –wave potential with electrode roughness, we were able to estimate the transfer coefficient $\alpha = 0.56$, while the usual approach using the Tafel slope from the current voltage relationship gives $\alpha = 0.46$, both for $z = 1$. This indicates a one electron process as rate determining step for the ORR in Ca^{2+} containing DMSO.

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Voltage-Controlled Formation of Silver Nanocap on a Gold Microelectrode for Efficient SERS of Monolayer Molecules

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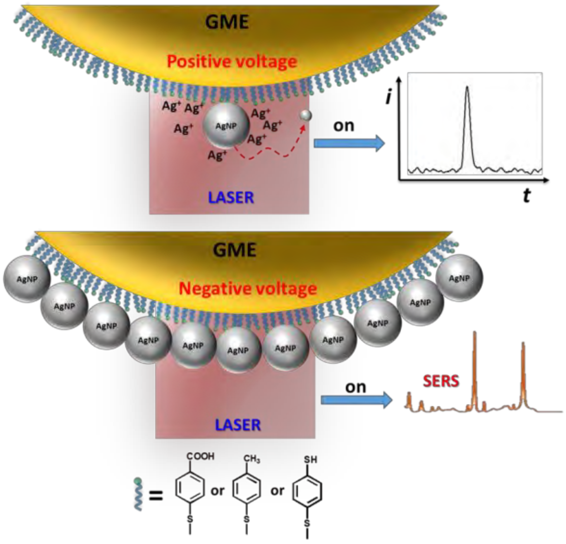
Abstract

Understanding of the chemical interaction and junction formation under molecule level brings remarkable interest to molecular electronics and molecular plasmonics,[1, 2] but still remains elusive. In this work, we studied the effect of the surface chemistry of the collector electrode on nanoparticle (NP) collisions and the molecular junctions through simultaneous electrochemical and surface-enhanced Raman spectroscopy (SERS) measurements. Different plasmonic molecular junctions were formed through the random collision events of silver NPs (AgNPs) in electrolyte with a gold microelectrode (GME) modified by benzenethiols with different terminal groups (-SH, -COOH and CH_3). As shown in the Scheme 1, when we applied a positive bias to a GME, due to the faradic oxidation of AgNPs, typical current spikes can be observed when a AgNP collides on the electrode surface. However, when negative bias was applied at the electrode, the AgNPs could stick on the electrode surface and formed the AgNP-on-GME geometry. The AgNP-on-GME geometry is analogous to the widely used "NP-on-Mirror" (NPoM) geometry,[3] in which extremely high Raman signal enhancement and single molecule sensitivity has been achieved due to the gap surface plasmon mode.[4] Moreover, different from NPoM approach, continuous bias can be applied in the AgNP-on-GME configuration. Using time-resolved electrochemical current measurement and SERS, we successfully observed the effect of various electrode surface chemistry on the transient electrochemical current changes and the evolution of newly formed molecular junctions through AgNP-GME collision events.



Scheme 1. Schematic diagram for the voltage-controlled formation of silver nanocap for efficient SERS of probe molecules on GME.

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Lithium-Sulfur Batteries: From Electrochemistry to Materials Practices

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Among various promising candidates with high energy densities, lithium-sulfur (Li-S) batteries with a high theoretical capacity and energy density are highly attractive;[1-2] while the commercial application of Li-S batteries still faces some persistent obstacles, such as the low electrical conductivity of sulfur and lithium sulfide and the dissolution of polysulfides. The introduction of nanocarbon into the field of Li-S batteries sheds a light on the efficient utilization of sulfur by improving the conductivity of the composites and restraining the shuttle of polysulfides. In this presentation, the concept for the rational design of nanocarbon for energy storage is explained. The advances in the use of advanced energy materials in the cathode, separator, and anode is explained.[3-14] New insights on the relationship between the nanostructure and the electrochemical performance are presented.

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Emerging Energy Chemistry of Li Metal Anode for Safe Batteries

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Li metal is considered as the "Holy Grail" of energy storage systems. The bright prospects give rise to worldwide interests in the metallic Li for the next generation energy storage systems, including highly considered rechargeable metallic Li batteries such as Li-O2 and Li-sulfur (Li–S) batteries. However, the formation of Li dendrites induced by inhomogeneous distribution of current density on the Li metal anode and the concentration gradient of Li ions at the electrolyte/electrode interface is a crucial issue that hinders the practical demonstration of high-energy-density metallic Li batteries.

In this talk, we review energy chemistry of lithium metal anode in safe batteries. Firstly, the importance and dilemma of Li metal anode issues in lithium–sulfur batteries are underscored, aiming to arouse the attentions to Li metal anode protection. Specific attentions are paid to the surface chemistry of Li metal anode. Next, the proposed strategies to stabilize solid electrolyte interface and protect Li metal anode are included. Finally, a general conclusion and a perspective on the current limitations, as well as recommended future research directions of Li metal anode in rechargeable batteries are presented.

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Electrochemically Assisted Surfactant Assembly in the hard X-ray beam: an in situ GISAXS study

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Under the Advanced Devices by Electroplating EPSRC programme grant (EP/N035437/1) we are working on the integration of nanowire semiconductor structures into electronics, using aligned mesoporous templates as host for the electrodeposition of high quality chalcogenide semiconductors. This necessitates the making of porous hosts for template electrodeposition, such as mesoporous silica structures. Mesoporous silica films are typically produced by evaporation-induced self assembly (EISA)[1], but vertical alignment of the pores to the substrate is very difficult to achieve. Hexagonal arrays of vertically aligned mesopores can be achieved by electrochemically assisted surfactant assembly (EASA)[2]. The self-assembly of a cationic surfactant (typically cetyltrimethylammonium bromide) close to the substrate surface relies on the application of a negative potential to an electronically conductive substrate, but also leads to the formation of spheroidal surface aggregates, limiting the obtainable film thickness to a few hundreds of nm[3,4]. Grazing incidence small angle X-ray scattering (GISAXS) allows for the non-destructive structural analysis of thin films with high statistical relevance in lateral and vertical direction. In this work, we show the results obtained from in situ GISAXS experiments done during the EASA of silica, following the evolution of the structure formation in real time with sub-second time resolution. From this, suggestions to a more detailed mechanism of formation are made.

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Cathodic Protection of 304SS Using Triboelectric Nanogenerator

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Metal corrosion has caused huge waste and serious threats to the economy and the safety of human life. Cathodic protection is the most commonly used method for metal corrosion protection in marine engineering, however it can cause waste of energy and anodes. In recent years, triboelectric nanogenerator (TENG) cathodic protection technology has shown good application prospects. In this work, polydimethylsiloxane (PDMS) and Al foil with different electronegativity were selected as the friction layer to construct a vertically separated TENG (PDMS-Al). In addition, the chitosan and AAO were used to topologically modify the PDMS and construct the micro-nano structure, and it was combined with Al to form PDMS/CS-Al and PDMS/CSr-Al TENG. The electrical output performance of TENG was evaluated. It was found that PDMS/CSr-Al TENG has better electrical output performance. The PDMS/CSr-Al TENG was selected to build a TENG cathodic protection system under the condition of simulating mechanical external force (Fig. 1). Driven by a simulated mechanical force of 5 Hz, it was found that the maximum output open-circuit voltage of the TENG can reach 77.1 V, and the surface potential of the exposed area of 1 × 1 cm^2 304ss can be reduced by about 0.1 V (Fig. 2), indicating that it forms a cathode for 304ss polarization protection. Furthermore, it explored and evaluated the application potential of TENG cathodic protection technology.

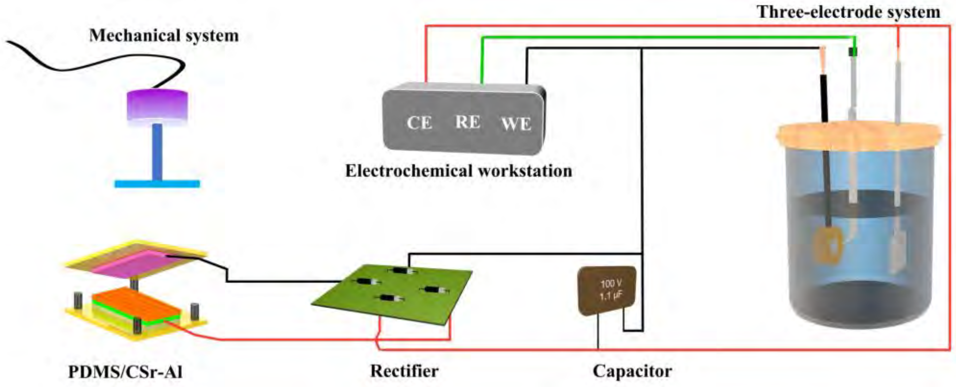

Fig. 1 PDMS/CSr -Al TENG cathodic protection 304ss system

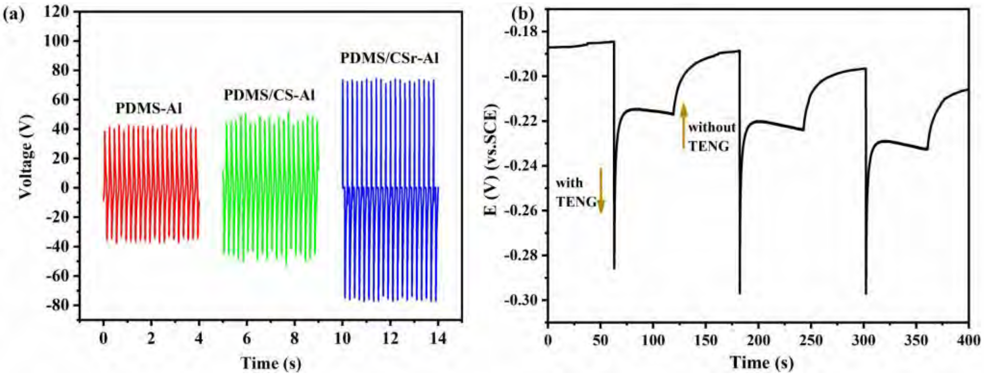

Fig. 2 Output performance curve of PDMS-Al、PDMS/CS-Al and PDMS/CSr-Al (a) output voltage (Voc); (b) Curve of 304ss OCP under PDMS/CS-Al TENG intermittent cathodic protection

VOCs abatement from gases streams by absorption enhanced with electro-scrubbing process

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Volatile organic compounds (VOCs) are characterized by their high activity in atmospheric photochemical reactions. In addition, human health can also be importantly affected, because VOCs can be easily absorbed by the skin and the mucosa, damaging the metabolic system and, in some cases, they can even be carcinogenic. Therefore, their removal is very important. A very promising technology for the treatment of gaseous polluted streams is electro-scrubbing [1], which consists of the combination of an absorption process with a mediated electrochemical oxidation. Its purpose is to retain gaseous contaminants into a liquid stream and then oxidize them using metal pairs as catalysts. This work focuses on the removal of toluene using a packed column and a one compartment electrolyzer. An electrolyte, based on the pair Co (II)/Co (III) in an acid medium, is used to capture toluene and degrade it. This electrolyte is circulated throughout an absorption column and the cell. The activation of the metallic catalyst and the efficiency in the contact between the phases are parameters that have been carefully analyzed. The recirculation of the washing solution through the electrochemical system allow the oxidant species to be regenerated and keep the treatment active. Reaction intermediates have been monitored by GC-MS and HPLC.

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Study of efficiency ozone electro-generation by PEM electrolyzers

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Ozone is a very powerful oxidant with many applications in water and wastewater treatment. Despite it is typically produced by non-electrochemical methods, its electrochemical production is becoming a topic of the major interest nowadays. Ozone can be generated by the oxidation of oxygen contained in water throughout different types of electrode materials and cell designs. Use of diamond anodes can be very important to reach high efficiencies in a process in which the low solubility of oxygen in water is one of the main drawbacks. To face this important problem, reactor design is very important and PEM electrolyzers seems to be promising options which allow the production of ozone at low voltages, and, hence, with high cost-effectivity. In this work, is evaluated the influence of pressure and use of mechanical microbubbles generators on the ozone electro-generation using different of PEM electrolyzers. Results highlight the great influence of these parameters which are of a great significance for the treatment of wastewater polluted with different organics, as it is also confirmed in different tests shown in this presentation.

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Generation of O_3 and H_2O_2 Using High-Pressure Electrochemical Reactor

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Ozone (O_3) and hydrogen peroxide (H_2O_2) are two environmentally friendly oxidants that have been used in several applications regarding wastewater treatment, purification of water loops used in the pharmaceutical and semiconductor industries, wood pulp bleaching process, treatment of textile wastewaters, and other applications [1]. It is well known that these two reactions can be performed in aqueous solutions by cathodic and anodic reduction using different cathodes and anodes, and using air coming from the air [2]. The performances of these two different reactions can be increased upon enhancing the pressure from 0 to up to 30 bar and, on the other hand, increasing the current density and modifying the composition of the electrolyte solution in which the reactions take place [3]. In this work, we have designed a reactor that works in high pressure conditions to facilitate the absorption of O_2 in an aqueous solution to react in an electrochemical reaction (Figure 1) using Boron Doped Diamond as anode material and PTFE-Carbon Black Reticulated Vitreous Carbon (RVC) as cathode material to achieve the production of O_3 and H_2O_2 in two different reactions, that would increase the efficiency using high-pressure conditions, using O_2 in a closed chamber. It is expected a dramatic effect of the pressure on the efficiency of these reactions, along with other parameters such as electrolyte composition, electrode materials and current density applied to the system.

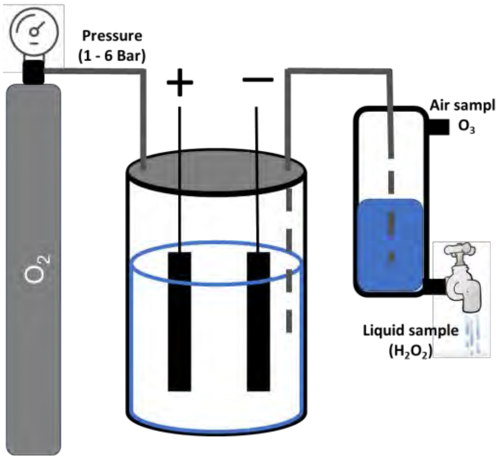

Figure 1. Schematic representation of the experimental setup to produce H_2O_2 and O_3 under pressure conditions.

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CO_2 Fixation via Carbonation of NaOH Generated by an Electrochemical Reactor

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The ability to convert carbon between different oxidation states in order to store and release energy relies on biological metabolism and in the center of human energy infrastructure and chemical industry. A potential approach to reduce CO_2 emissions and fossil-fuel consumption that has attracted nowadays attention is the recycling of CO_2 into fuels and chemicals [1]. One of the several strategies to mitigate CO_2 emissions is Electrochemical CO_2 reduction (CO_2R), these processes for the fixation of CO_2 have been the focus of many research activities mostly for the necessity of dealing with the increment of this compound in the atmosphere, which is correlated with global warming and pollution in many industrialized countries and worldwide [2]. Carbon atoms in CO_2 molecules are in their highest oxidation state, whereas those in common fuels and chemicals such as hydrocarbons, alcohols, and acids are in lower states, and for the synthesis of these compounds an energy input is required, which is one of the main reasons why CO_2 is not extensively used in current chemical industries [3]. In this work, we aimed to fixate CO_2 in an adsorption glass column coupled to an electrochemical reactor (Figure 1), which consists of two electrode chambers separated by an ionic membrane, that produces Cl_2 in the anode (MMO) chamber and NaOH and H_2 in the cathode chamber (stainless steel), which is connected to the adsorption column to generate $NaCO_3$ and $NaHCO_3$. Our results show that CO_2 fixation in this reactor depends on the electrolyte concentration, the intensity applied, which is correlated to the amount of NaOH and Cl_2 electrogenerated in both chambers, and on the velocity and concentration of CO_2 that is injected to the adsorption column. This technology can be used to produce secondary added value products (hydrogen, chlorine) and help to mitigate CO_2 emissions.

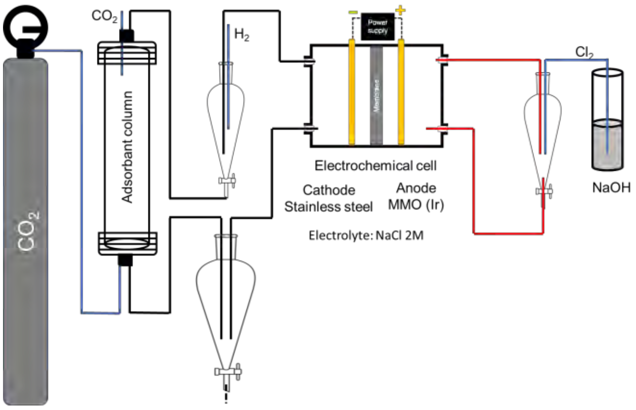

Figure 1. Schematic representation of the electrochemical reactor coupled to a CO_2 fixation column.

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Impedance Measurements on QLED Devices: Analysis of High-Frequency Loop in Terms of Material Properties

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Quantum-dot light-emitting diodes (QLED) are used in the new generation of electronic displays. A QLED based display can offer superior performance, including brightness, color purity, color gamut, and efficiency, at a lower cost as compared to existing technology. Electrochemical impedance spectroscopy (EIS) has been applied over the decades to study the light-emitting diode (LED) devices and could provide an ability to characterize the electrical properties of the material. However, work is needed to improve the interpretation of the EIS response of QLED devices.

Constant-phase-element (CPE) behavior is often observed in EIS response of electrochemical and solid-state systems. The CPE can be used to improve the fit of the equivalent circuit model to the impedance data. However, interpretation of the CPE parameters to extract physical meaning requires an understanding of the time-constant distribution in each individual system. Hirschorn et al.[1,2] developed a power-law model that could relate the CPE parameters to the physical properties of the film by regression of the measurement model[3-5] to synthetic data. The distribution of resistivity was identified by assuming a uniform dielectric constant.

The objective of the present work is to interpret the high-frequency impedance response on red and green QLED devices in terms of the physical properties of the device. Impedance measurements were performed on red and green QLED devices under current densities chosen to yield specified luminescence. A circuit model was developed for the observed high-frequency loop in terms of the thickness, dielectric constant, and resistivity distribution of the hole-injection layer. dielectric constant and resistivity were extracted with a known layer thickness obtained from Scanning Electron Microscopy (SEM) analysis. Impedance measurements performed on hole-transport only devices were used to verify the interpretation of the high-frequency capacitive loop in terms of the properties of the hole-injection layer.

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Acknowledgement

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Investigations on the vanadium ion reaction kinetics on single carbon fibre electrodes

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The vanadium redox flow battery (VFB) is a promising energy storage system, due to its durability and intrinsic safety. Several studies on the kinetics of the VFB reactions are already available, however mainly on model electrodes such as platinum or glassy carbon [1]. The kinetics at these model electrodes can deviate significantly from real electrodes, since different overpotentials and reaction mechanisms might occur. Besides that, the electrode structure of real materials is neglected when using model electrodes.

For understanding the interplay between the electrolyte and the electrode, investigations on commercial electrode materials, such as porous carbon felts are necessary. Because of the complex structure of the porous electrodes, especially due to the strong influence of the morphology and pore volume on the results, the interpretation of the electrochemical data is highly complex [2]. In addition, the low conductivity of the electrolyte results in inhomogeneous current density distributions in the porous electrode, which makes an exact determination of kinetic parameters very difficult [3].

Therefore, neither a model electrode nor a complete commercial porous electrode was applied in our studies. Instead, we used single carbon fibre microelectrodes (similar to [4], see figure 1, left), which were detached from commercial electrode materials, connected to a copper wire and isolated with a heat-shrink tubing. These electrodes were operated under technically relevant electrolyte concentrations and examined by electrochemical impedance spectroscopy (EIS) and polarization curves. The results were used to determine the reaction rate constants, the transfer coefficients, and the reaction orders of the vanadium ion reaction kinetics. For example, the exchange current density was determined depending on the state of charge of the electrolyte (see figure 1, right). In addition, different fibres out of one single piece of electrode were investigated to analyze the variation of kinetic activity within the material, which can occur due to irregularities in the production process or during activation.

The gained precise kinetic parameters allow to improve electrode materials for VFB. Furthermore, they are useful for electrode models, which are applied to study the influence of mass transport and current density inhomogeneities in porous electrodes. Thereby, the influence of activation methods on the electrode materials can be investigated and better understood.

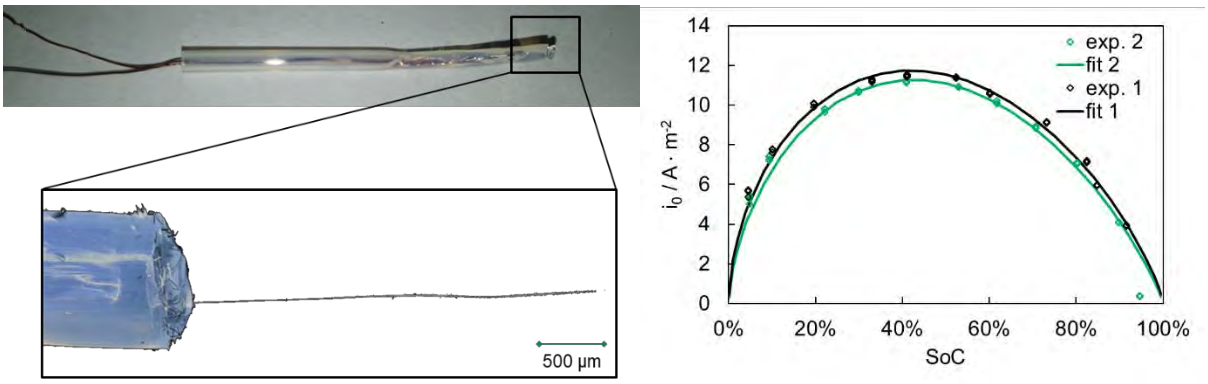

Figure 1: Carbon fibre microelectrode (left) and experimental results from two subsequent experiments in negative electrolyte compared to mathematical fit of reaction order (exchange current density at different SoC).

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Silicate Ions as Inhibiting Agents for Reinforcement Steel

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Reinforced concrete is a reliable building material due to many excellent properties such as strength and durability. However, marine environments and chloride-contaminated aggregates accelerate deterioration and failure[1]. Inorganic inhibitors are frequently considered to mitigate steel corrosion [2,3]. In this work, silicate ions were tested as corrosion inhibitors in concrete pore simulating solutions contaminated with chloride ions. The electrochemical evaluation included cyclic voltammetry and polarization curves. Weight loss tests were implemented to follow the inhibitor performance over long exposure times. Micro-Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to investigate the composition of the surface film.

Steel is tested in an alkaline solution simulating the composition of pore solutions in concrete (pH 13) contaminated with 0.3 mol/L chloride ion, which also contains 0.3 mol/L silicate ion (Cl-PSS-Inh). Compared to Cl-PSS, the improvement in behavior and the difference in response when silicate ions are present is clear from the results of all the techniques used to evaluate the electrodes.

Anodic polarization curves show no sign of pitting or any form of localized corrosion and very low passive current densities when silicate ions are present in solution. These results are promising in terms of the ability of these inorganic ions to be used as corrosion inhibitors.

When chloride and silicate ions are present simultaneously in an Inhibitor/Chloride = 1 ratio, complete inhibition of the localized attack is observed after 60 days of immersion.

Cyclic voltammograms and XPS spectra indicate that the presence of silicate ions affects the composition of the passive film (see Figure 1). However, further study is needed to understand the mechanism of action of silicate ions as inhibitors and to explore their effectiveness when used in mortars, concrete or to pre-treat the steel bars.

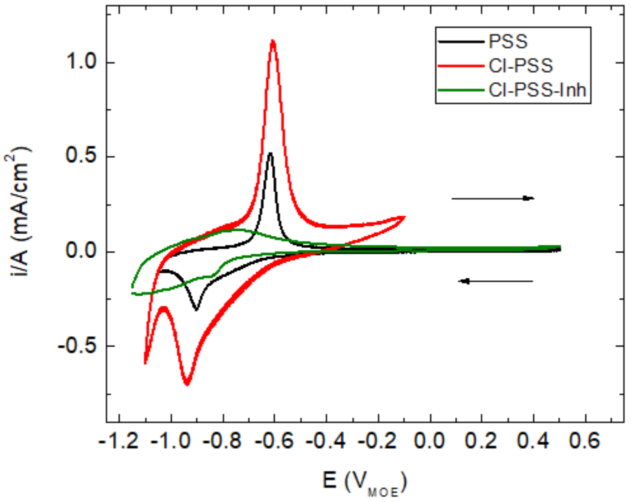

Figure 1: Cyclic voltammograms recorded for steel in pore simulating solutions (pH=13) showing the effect of chloride ions and chloride plus silicate ions. Silicate ion concentration is 0.3 mol/L and Inhibitor/Chloride = 1. Scan rate = 10 mV.s^{-1}. The tenth cycle is presented.

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Recurrence Quantification Analysis as a Tool to Investigate Current Oscillations Observed During the Mass-Transport Controlled Electrodissolution of Fe in Sulfuric Acid Solutions

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Recurrence is a fundamental property of nonlinear dynamical systems, which can be utilized in order to characterize the system dynamics in phase space. A visual tool for exploiting the recurrence behavior of phase space trajectories is the recurrence plot (RP) introduced in 1987 by Eckman et al [1]. On the basis of the RP, recurrence quantification analysis (RQA) can be carried out to identify different dynamical regimes and characterize transitions between them. Recurrence plots (RPs) and recurrence quantification analysis have been widely used in many scientific fields from chemistry, physics and engineering to life sciences, ecology and economy [2, 3]. RQA was also turned out to be a key issue revealing complex dynamics, phase and generalized synchronization in non-phase-coherent and even non-stationary time series of electrochemical systems and characterizing different corrosion states of metals and alloys [4-6]. This study aims in exploring non-linear quantifiers based on RPs and RQA in order to investigate complex current oscillations observed during the mass-transport controlled electrodissolution of iron in sulfuric acid solutions (Fe|0.75 M H_2SO_4 interfacial system). Under the potentiodynamic operation mode, Fe|0.75 M H_2SO_4 is a well-known electrochemical system exhibiting multiple oscillatory potential regimes depending on various control parameters [7]. Our focus here is on oscillations appeared in the limiting current region beyond a critical value of the ohmic potential drop and when proper hydrodynamic conditions are established across the interfacial region [8]. By applying two system configurations comprising an upward and a downward-facing Fe-disc electrode, visual changes in RPs plots and RQA measures, such as the average diagonal line (ADL), the trapping time (TT) and the longest vertical line (LVL) along with a new entropy quantifier, reveal different nonlinear correlations. The new entropy quantifier was based on recurrence matrix microstates that represent more general properties of the recurrence space as compared with the entropy quantifier based on just diagonal or horizontal lines of the recurrence space [9]. Indeed, the microstate-based entropy quantifier reflects correctly the system complexity in agreement with ADL, TT and LVL. All RQA measures indicate that the enhancement of the mass transfer affects the complexity and the transitions between different nonlinear dynamical regimes.

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Tailored lipidic liquid crystalline phases and their nanoparticles as carriers of doxorubicin and ^{177}Lu – drug release studies by voltammetry

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The long-term use of conventional chemotherapeutics leads to damage of healthy cells and adverse side effects. To minimize the side effects of the drugs, achieve their sustained release or improve their stability they can be delivered encapsulated in appropriate drug carriers. Here we propose tailored liquid crystalline structures (LCP) and their nanoparticles (LCNP) that incorporate an anti-cancer drug together with complexed radioconjugates in order to obtain more effective action towards the cancer cells.

Lipidic liquid-crystalline phases, such as cubic phases, are promising as drug carriers since they have large interfacial area of 400 m^2/g and their structure consists of bicontinuous lipid bilayer surrounding two systems of non-contacting aqueous channels. A wide range of drugs can be encapsulated in this biocompatible amphiphilic environment resembling that of a biological membrane. Cubic phases are stable in the excess of water and can be dispersed in the presence of stabilizer into colloidal nanoparticles – cubosomes. Cubosomes are less viscous and exist as a suspension which makes them easier to handle and deliver to the appropriate site.[1-4]

We prepared cubic phases and cubosomes with doxorubicin (DOX), a drug with particularly negative side effects, and we characterized the mesophase structure by small angle X-ray scattering (SAXS) and DLS (for cubosomes). To investigate the behavior of the drugs incorporated in the carrier and to determine drugs release profile we used electrochemical methods and UV-Vis spectroscopy. We considered Korsmeyer-Peppas and other mathematical models in the evaluation of the drug release kinetics. In order to obtain more effective action, the cubosomes containing DOX were also doped with an amphiphilic ligand complexing ^{177}Lu radionuclide. We used MTT assay to evaluate cytotoxic effect of the cubosomes with single and two components upon selected cancer cell lines.

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The Redox Reactions of V(III)/V(II) and V(V)/V(IV) Couples in all-Vanadium Redox-Flow Battery Electrolyte: the Importance of Glassy Carbon Electrode Pre-treatment

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Vanadium-redox-flow batteries (VRFB) have been intensively developed and commercialized since the last decade. This electrochemical processes in VRFB are based on conversions of vanadium redox couples in highly acidic media: V(III)/V(II) at the anolyte and V(V)/V(IV) at the catholyte. In practice, the kinetics of both of these reactions are known to be sensitive to the electrode pretreatment. For this reason, the widely used graphite felt electrodes for VRFB usually undergo thermal pre-oxidation or oxidative chemical pretreatment. However, the detailed mechanism of these electrode reactions is unknown and the interpretations of the effect of electrode surface pre-treatment are controvercial[1].

n this work we present the compairison of the literature data on the kinetics of the V(III)/V(II) and V(V)/V(IV) electrode reactions, considerations about the effect of the electrode surface and the cyclic voltammetric experimental data at glassy carbon electrode material. Special attention is given to the pre-treatment protocol. To characterize the state of the electrode surface, the potassium hexacyanoferrate is used as a reference redox-active probe.

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Electrochemical impedance spectroscopy protocol for detection of Norfloxacin at a polyamic acid modified electrochemical sensor

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Pharmaceuticals are introduced into the environment through many different pathways including production and consumption waste, ineffective water treatment, improper disposal of even as unused pharmaceutical waste. Pharmaceutical contaminants are on the WHO critical list as priority emerging pollutants in water, since in many countries, disposal remains unregulated. Norfloxacin is a hemotherapeutic antibiotic agent which is used to treat urinary tract infections and respiratory infections, among others. Due to the high water solubility required of antibiotics, antibiotics are able to pass through all the typical filtration systems employed in water treatment plants and reach surface water, groundwater and even drinking water.

Electrochemical sensors are devices that change electrochemical information into an analytical signal that is useful for quantification. Conducting polymers are widely used as transducers in the design of chemical sensors, however they have some disadvantages such as low sensitivity, poor selectivity and surface poisoning due to adsorbed intermediates or interfering species. The aromatic polyimides typically exhibit good thermal and chemical stability, mechanical strength, and low dielectric constants. Among them, polyamic acid (PAA) was used for different applications, including sensor modification. PAA is a polymer with cation complexing properties, due to its carboxyl groups. Integrating metal nanoparticles into polymers to form polymer nanocomposites tends to improve the physical and chemical properties of the sensor. The unique optical, electrical, magnetic and catalytic properties of cobalt nanoparticles have made desirable in applications of nanoelectronic devices, nanosensors and catalysts. In this work we have shown how the unique combination of Co-nanoparticles incorporated into a deposited polyamic acid thin film has been advantageously employed for the sensitive detection of Norfloxacin. Following the use of a variety of techniques including microscopy and small angle X-ray measurements to verify the topography and morphology of the sensing layer, electrochemical impedance spectroscopy was employed to extract the mechanism of interaction between Norfloxacin and the modified transducer.

Nanostructured Silicon as Anode for Lithium-ion batteries

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The enhancement in the morphology of anode materials leads to better capacitance properties. Nanostructure design is an effective way to improve battery cycling because nanostructures provide short diffusion length for Li$^+$ ions and electrons with better resistance to fracture [1]. The most widely used anode is graphite whose lithiated compounds have stable phases up to the LiC$_6$ stoichiometry corresponding to a theoretical specific capacity of 372 mAh / g [2]. In contrast, silicon possesses a very high theoretical capacity of 4200 mAh / g and can intercalate 4.4 Li into Si at high temperature to form Li$_{15}$Si$_4$ [3]. Silicon also features a working potential around 0.4 V vs. Li / Li$^+$ which is safer than operating potential of graphite (0.05 V vs. Li / Li$^+$). Although silicon possesses all of these advantages, silicon-based anodes suffer from huge volume expansion upon cycling (≈400%) causing electrode fracture and electrical isolation during repeated cycling [4]. Continuous volume changes cause the breaking-reformation of the solid electrolyte interphase (SEI) film which leads to the consumption of lithium-ions and electrolyte.

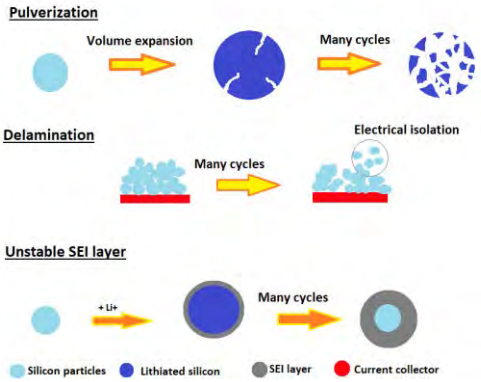

Fig. 1 Cell failure mechanisms of silicon

There are two strategies to avoid this problem, first one is combining Si with different kinds of carbon materials such as amorphous carbon, conductive carbon black, carbon nanotubes and graphene and secondly, by designing nanoscale silicon with different structures. In the present work, we represent nanostructured composite anodes. Structural and microstructural changes in silicon nanomaterials were examined using several methods: X-ray powder diffraction combined with the results of Raman spectroscopy, FT-IR spectroscopy, UV-Vis spectrometry, Nitrogen adsorption measurements, and TEM analysis. Electrochemical performances were investigated by cyclic voltammetry and galvanostatic charge-discharge measurements.

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Mechanically interlocked carbon nanotubes as versatile and stable platform for nano electrocatalysis

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One promising way to store and distribute renewable energy like solar and wind energies is the electrochemicals production of fuels like hydrogen (H_2), hydrogen peroxide (H_2O_2) and methane (CH_4)[1]. The reported most promising electrocatalysts are based on rare and expensive noble metals as they are highly efficient and stable, therefore the recent researches have been focusses on the substitution of noble metals with earth abundant elements[2,3] or metal-free catalysts[4,5]. A major drawback of currently available electrocatalysts for the large-scale application, is poor long-term stability due to decomposition or delamination. To overcome those limitations, mechanically interlocked carbon nanotubes (MINT) has been investigated due to its strong immobilization of the organic compound in a rotaxane-type while still maintaining the desired properties of the carbon nanotube as well as the organic catalyst.

The successful synthesis and characterization of non-covalent rotaxane-type MINT with various organic molecules was demonstrated[6]. Motivated by tunable chemical catalytic capability of anthraquinone MINT's (AQ-MINT)[7], we investigated AQ-MINT as an electrocatalyst toward oxygen (O_2) to H_2O_2 reduction, as quinones in general are known for their capability of O_2 to H_2O_2 transformation[8].

This work studied the electrochemical behaviour of AQ-MINT's in comparison to supramolecularly adsorbed species (AQ@SWCNT) in aqueous and organic solutions[9]. Thereby, the versatility as well as superior stability of the MINT immobilization could be demonstrated. Furthermore, the electrocatalytic O_2 reduction to H_2O_2 was studied in neutral and basic aqueous media over 8 h. The results revealed that oxygen was reduced electrochemically using AQ-MINT in basic solution yielding 7.0 µmol of H_2O_2 after 8 h electrolysis, which correspond to a maximum catalytic activity of up to 12 $\mu mol_{(H2O2)}\ mg_{(AQ\text{-}MINT)}^{-1}\ h^{-1}$ or a turnover number (TON) of 417.

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Templated Electrodeposition of Nanoscale p-Block Materials

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Our project (ADEPT, EPSRC EP/N035437/1) aims to intergrade electrodeposition into device fabrications including thermoelectric devices, infrared detectors and phase change memories. This work focuses on producing nanowires by templated electrodeposition, the schematic is displayed in Fig 1. Silica thin films with well-ordered three-dimensional (3D) mesoporous structures were used to be the templates for electrodeposition. They were synthesised by evaporation-induced self-assembly (EISA) process using Pluronic F127 triblock copolymer as a structure-directing agent. FE-SEM showed that most of the pore diameters were between 6 and 10 nm. Grazing incidence small-angle X-ray scattering (GISAXS) showed that pore structure of the template adopted Fmmm space group with [010] orientation, as shown in Fig 2 (a). Bismuth and tellurium were grown through the 3D mesoporous channels by conducting two-step pulsed electrodeposition in a non-aqueous electrolyte system. Fig 2 (b) shows the Te nanowires grow through the mesostructure of the silica films. Electrodeposition conditions were controlled to optimise the nucleation and growth process and to maximise pore filling. *In-situ* grazing incidence small-angle neutron scattering was used to follow Bi electrodeposition into the pores and to link variations in nucleation to differences in the grown material.

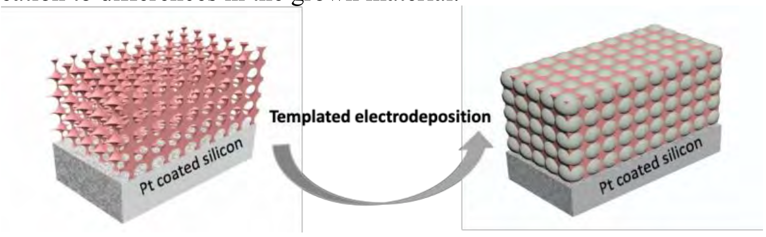

Fig 1 The schematic of templated electrodeposition

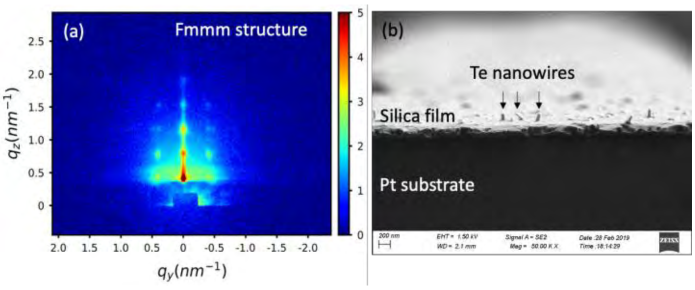

Fig 2 (a) The GISAXS pattern of the silica film as the template; (b) The cross-view SEM image of Te nanowires grow through mesostructure of the silica film.

An additional mechanism of extracellular electron uptake by microorganisms: Can the maintenance of low H_2 partial pressures favor the H_2 reaction on a cathode or metallic iron?

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Several anaerobic microorganisms, e.g. acetogenic bacteria and methanogenic archaea, are capable of using solid electron donors, such as a cathode or metallic iron (Fe(0)). Such microorganisms are of interest for novel applications such as microbial electrosynthesis (cathode as electron donor), while they could also cause detrimental microbial induced corrosion (Fe(0) as electron donor). Intriguingly, similar microorganisms can differ strongly in their capacity to use solid electron donors, which likely relates to their extracellular electron transfer (EET) mechanism. Different EET mechanisms have been proposed for acetogens and methanogens (Figure). Recently, I proposed an additional mechanism: the maintenance of low H_2 partial pressures by microbial H_2 consumption, which thermodynamically favors the H_2 evolution reaction on the cathode or Fe(0) surface (Philips, 2020). I will elaborate in my presentation how H_2 consumption affects the H_2 evolution on a cathode, as well as the anoxic corrosion reaction. In addition, I will discussed that microorganisms strongly differ in their H_2 consumption characteristics. Furthermore, I will explain my hypothesis that the difference in the capacity of microorganisms to use solid electron donors is likely related to differences in their H_2 consumption characteristics. Finally, I will discuss how the EET mechanism I propose relates to other EET mechanisms. My presentation will mainly focus on acetogenic bacteria, but similar considerations are also relevant for other hydrogenotrophic microorganisms.

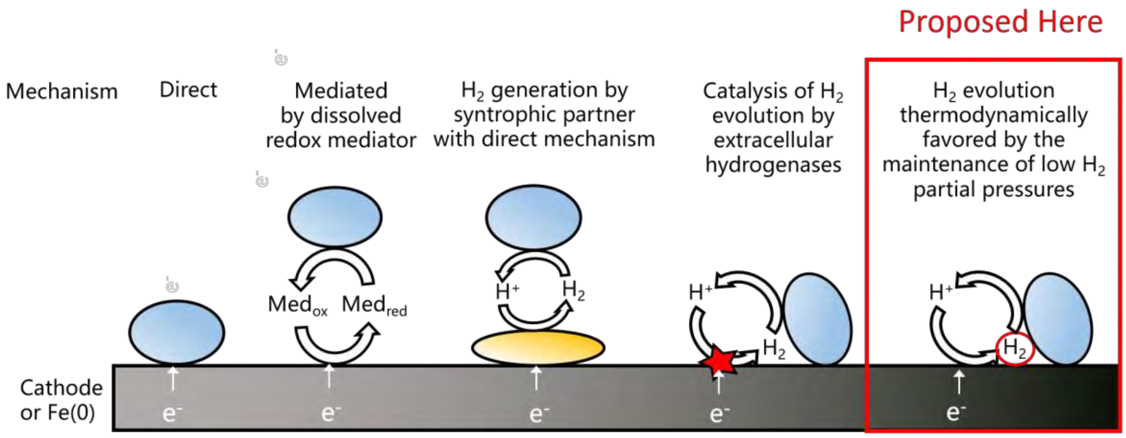

Figure: Overview of the different EET mechanisms previously proposed for microorganisms capable of using a cathode or Fe(0) as electron donor and the additional mechanism that I will discuss (Figure adapted from Philips (2020))

Reference

Philips J (2020) Extracellular electron uptake by acetogenic bacteria: Does H_2 consumption favor the H_2 evolution reaction on a cathode or metallic iron? *Front Microbiol* **10**: 13.

Electro-Fenton process combined with anodic oxidation at sub-stoichiometric titanium oxide (Ti_4O_7) ceramic electrode for the mineralization of tetracycline

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Keywords: Tetracycline, anodic oxidation, electro- Fenton process, Ti_4O_7-ceramic anode, carbon felt, TOC removal efficiency

ABSTRACT

The exploration of electrochemical advanced oxidation processes (EAOPs) have become popular for the degradation of pharmaceutical pollutants in wastewater treatments. This work investigated the degradation of tetracycline (TC), toxicity and intermediate studies using EAOPs. Carbon felt and Ti_4O_7 layer deposited on Ti substrate were used respectively as cathode and anode. Electro-Fenton (EF), anodic oxidation (AO) and electro-Fenton coupled with anodic oxidation (EF/AO) systems were used to degrade TC and their performances were compared. EF/AO performed most efficiently, with removal efficiency of 64.89±0.17% and 68.27±0.43%, at 20 ppm and 50 ppm TC, respectively, as compared to EF and AO. Then different applied currents were investigated for 20 ppm and 50 ppm TC, using EF/AO. Optimal conditions were established for 20 ppm and 50 ppm TC to investigate the intermediate products using HPLC and toxicity tests. The toxicity of the solution was less than initial stage of treatment, corresponding to the formation of less toxic by-products. EF/AO process using Ti_4O_7 anode and CF cathode provides low energy and high mineralization current efficiency (MCE) with high removal efficiency, because of the production of hydroxyl radicals at the surface of the anode and also a large surface area and porosity of CF. The ceramic sub-stoichiometric Ti_4O_7 anode with CF (EF/AO) can be used to degrade pharmaceuticals successfully.

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Electrochemical pressure impedance spectroscopy applied to polymer electrolyte membrane fuel cells: investigation of diffusion and water transport

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The polymer electrolyte membrane fuel cell (PEMFC) is a simple power device but inside it a complex and coupled mass transport phenomena are key factors in governing its performance and durability [1]. Over operation time membrane electrode assembly degrades, the diagnosis is usually done by a popular technique called electrochemical impedance spectroscopy (EIS). It gives out information on the cause of degradation, but it fails considerably to comment on and distinguish between mass transport processes with comparable time constants [2]. The PEMFC offers gas pressure as a non-electric variable to observe. When combined with current or voltage it gives us additional definitions of impedance and using this technique in harmonic conditions is called electrochemical pressure impedance spectroscopy (EPIS) [3,4].

Niroumand et al [5], made the first attempt to analyze the dynamic relationship between pressure and voltage by examining pressure-induced voltage oscillations in polymer electrolyte fuel cells. It has been demonstrated that cell voltage exhibits oscillations with an identical frequency of the cathode outlet pressure modulation and concluded that a spectrum of such relationship over a range of 0.1 Hz to 20 Hz frequency can be used as a diagnostic tool to understand transport processes such as water transport, limitations in electrode gas flow transport. Hartmann et al [4] applied EPIS to sodium-oxygen batteries by monitoring pressure amplitude in relation to electric current and obtained vital information about hydration imbalance, changes in reactant distribution, their effects on mass transport and concluded that EPIS was significantly sensitive to oxygen transport properties of porous electrodes. In addition, Rho et al. [6] showed that the significant control by diffusion of the reacting gas in the inert gas can be specifically examined by comparing the phase shift of the system with inert gas-oxygen mixture (e.g. air) to that with pure oxygen.

In this work, the focus is on applying EPIS to PEMFC and developing it for better understanding the transport process having comparable time constant inside PEMFC. A sinusoidal variation in the cathode backpressure was applied and the voltage response of the fuel cell was recorded at constant current in a frequency range of 1 mHz to 1 Hz with pressure amplitudes of a few mbar. In order to better resolve the transport processes, experiments with varying oxygen mole fraction were carried out. It was observed that the impedance modulus decreases rapidly with increase in oxygen mole fraction (beyond 0.4) and it is the lowest in case of pure oxygen. In case of pure oxygen, it was observed that the absence of nitrogen contribution in diffusion causes the overall impedance to reduce dramatically over whole spectrum and phase shift in low frequency region (below 50 mHz) depicting the detection of diffusion when compared to air. These observations about oxygen sensitivity are in accordance with results obtained by Hartmann et al [4] and Rho et al [6]. Experiments with reduced stoichiometry of pure oxygen at high polarization and 100 % RH are underway for possible detection of flooding by EPIS, enabling the proper resolution of the diffusion and water transport inside PEMFC.

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Electrochemiluminescence – Counter Claims

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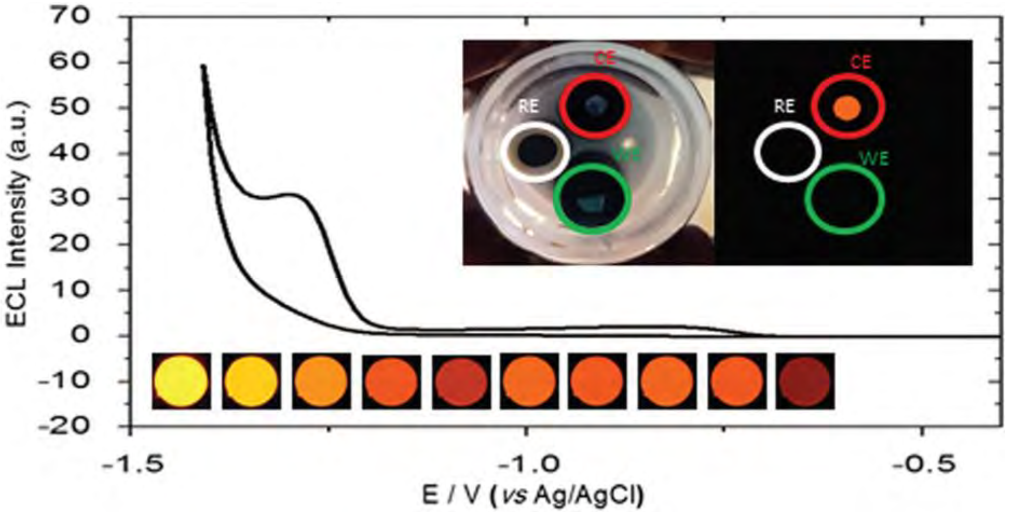
Electrochemiluminescence (ECL) analytical applications have been increasingly exploited in recent years. The majority of these applications are based upon the tris(2,2'-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$ system with various secondary or tertiary alkylamine co-reactants such as tri-*n*-propylamine (TPrA) which generally follows the oxidative-reductive or anodic co-reactant ECL mechanism.[1,2,3] However, the mechanisms at the counter electrode have largely been ignored. This offers a unique opportunity to further exploit ECL based systems, particularly for multiplexed analysis, by examining the electrochemical processes occurring at the counter electrode. Indeed, this work highlights the importance of considering this in the elucidation of ECL reaction mechanisms. Not surprisingly, the processes observed at the counter electrode were dependent on the configuration of the electrochemical cell, as (i) the voltage at the counter electrode is adjusted by the potentiostat to account for any change within the system to maintain the desired potential at the working electrode, and (ii) the position and geometry of the counter electrode will determine the portion of emitted light that is measured by the photodetector.[4]

Beyond the implications for investigation into ECL reaction mechanism, the recognition of processes at the counter electrode resulting in intense ECL and the development of our instrumental approach to distinguish the source of the emission creates exciting possibilities for analytical applications involving a dual ECL response at the working and counter electrode. A new approach to examine electrochemiluminescence (ECL), in which the potentials at both the working and counter electrodes are measured and the emitted light is detected by a photomultiplier tube, camera and then a charge-coupled device (CCD) spectrometer, provides unequivocal evidence that the purported cathodic ECL of [Ru(bpy)3]2+ and tri-n-propylamine actually arises from anodic reactions at the counter electrode.



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Synthesis and electrocatalytic reduction of CO_2 on nanostructured materials

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Fossil fuels accounts for a large portion of the total energy required for human beings over the past decades as they produce higher current density than other energy systems, resulting in an exponential growth in CO_2 emission to the atmosphere. This causes environmental pollution as CO_2 is considered to be one of the major contributors to global warming. On the other hand, CO_2 is also an essential material for the growth of all plants and many industrial processes. In order to maintain the ecosystem stability, the total release of CO_2 in the environment by all sources should be balanced with what is consumed in an ideal scenario. Considering the worldwide total energy consumption trends, it is challenging is to stop using fossil fuels until environmentally clean energy systems are invented and adopted. Another possible approach is to capture and sequestrate CO_2 geologically or to convert CO_2 into useful chemicals such as low-carbon fuels. All over the word, many research groups are working on green technologies for the environmental friendly energy such as solar, wind, tidal and biomass energies whereas other research groups throughout the world are attempting to convert CO_2 into useful chemicals such as H_2, HCHO, HCOOH, CH_3OH, C_2H_5OH, CH_4 and CO with photo- or electro-catalysis and others or to capture and sequestrate with different adsorbents.

Herein, I plan to discuss the novel strategies adopted for synthesizing nanostructures for metallic and bimetallic catalysts and their performance for electrocatalytic reduction of CO_2. Some selected catalysts are also evaluated for thermal catalysis to compare the differences in activity and the nature of product when two different platforms are used. Catalysts are primarily composed of transition metals and their alloys (Cu, Ni, Zn, Co etc. and alloys with Ag). Combustion synthesis, hydrothermal techniques and galvanic exchange methods were adopted to fine-tune the surface and structure of the catalysts [1,2]. Some selected catalysts, e.g. Ni, Cu and Ag, were also deposited on fumed silica and calcined at high temperature to obtain supported catalysts for thermal-catalytic reduction of CO_2 [3]. Electrocatalytic results indicate selectivity towards formic acid, and formate species; whereas thermal catalytic results show a greater tendency towards methane and CO formation. All the catalysts were characterized in detail using XRD, XPS, SEM/TEM before and after the reaction to understand the structural changes owing to the reaction. Reaction pathway studies were also performed by using in-situ FTIR studies in DRIFTS mode to monitor the reaction intermediates with temperature.

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Influence of Aspect Ratio on the Current Density Profile of Recessed Stimulation Electrodes

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Introduction Electrical stimulation is a therapeutic technique aiming at restoring impaired biological functions by injecting a controlled amount of charge in the body. Commonly used planar stimulation electrodes exhibit a non-uniform current density distribution (j) that can lead to locally exceeding the safe stimulation threshold[1]. An electrode can be recessed into an insulating part, which results in a different j [2], thus a different injection of charge, which can induce damage or insufficient stimulation. However, few studies[3] have focused on the influence of the recess parameters on j and how it could be used in electrode design. *Material & Methods* A finite element model was used to calculate j at recessed and non-recessed planar disc platinum electrodes in saline in response to an applied potential (COMSOL 54 Electrochemistry module). Recess shape (tubular and conical) and aspect ratio (AR), defined as recess depth divided by electrode diameter, were varied. Fig. 1 (c) shows a transverse view of a conical (left) and tubular (right) recess with the electrode covering the entire base of the recess. *Results* The tubular recess presents a uniform j at the electrode surface and at most depths throughout the recess, except at the open end of the recess, where the apparent j is more similar to the one of a non-recessed electrode, fig. 1(a, c). The conical recess presents a distribution more similar to a non-recessed electrode at the electrode surface, which becomes more uniform towards the recess end, fig. 1 (b, c). Increasing the AR makes j more uniform, both at the electrode surface and at the end of the recess, fig. 1 (a, b, d). At a given AR, varying the dimensions of the recess does not affect j, with relative standard deviations typically smaller than 0.5% (7 ARs tested, 3 pairs of dimensions per AR). *Discussion* The non-uniformity of j depended only on the recess shape and AR. Understanding this relationship will allow finetuning the current density profile at the electrode surface and at the recess end. For instance, a tubular recess with an AR larger than 2 will yield a uniform distribution at the electrode surface. Similarly, a conical recess of AR = 1/3 will reproduce the current density profile of a non-recessed electrode with less than 6% error, while being straightforward to manufacture. This study used a purely resistive model under steady-state conditions, which is a simple model for charge injection at an electrode-electrolyte interface. Further studies will consider a more realistic charge-transfer model and conditions closer to real dynamic electrical stimulation experiments.

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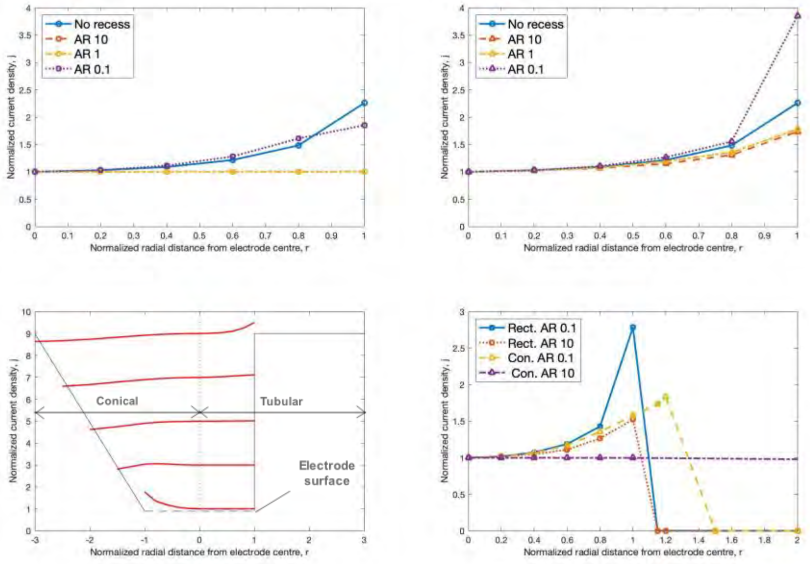

Comparison of Electrocatalytic Properties of $AuCo_3O_4/C$ and $PtCo_3O_4/C$ Catalysts towards alcohols oxidation reaction

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In recent decades, direct alcohol fuel cells have been interested due to their advantages over hydrogen fuel cell. Alcohols such as methanol, ethanol and ethylene glycol are the most common types of fuel used in direct liquid-feed fuel cells. Moreover some of fuels are especially attractive as they can be produced from renewable biomass. Main advantages of liquid, low-molecular weight alcohols as fuel are that they can be easily handle storage and transported compared with hydrogen fuel.

One more important thing is research based on the development of new, various rare earth metals and metal oxides compositions, the improvement of known materials such as carbon with various additives with the aim to reduce or completely refuse of noble metal and to find low cost, more efficient and greater performance catalysts. Nanoparticles-based catalysts are usually heterogeneous catalysts broken up into metal nanoparticles in order to speed up the catalytic process. Metal nanoparticles have a higher surface area so there is increased catalytic activity because more catalytic reactions can occur at the same time. Pt is known as one of the best electrocatalysts for alcohols oxidation. However, among the many various catalysts studied for oxidation of alcohols in alkaline media Au was noticed to have high electrocatalytic activity towards the oxidation of alcohols and great tolerance for surface poisoning.

This paper presents comparison of electrocatalytic activities of $AuCo_3O_4/C$ and $PtCo_3O_4/C$ catalysts towards methanol, ethanol and ethylene glycol oxidation reactions in an alkaline medium. The Au and Pt nanoparticles were deposited on the Co_3O_4/carbon (Co_3O_4/C) substrate using microwave irradiation method. The composition, morphology and structure of the prepared catalysts were characterized using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and X-ray diffraction (XRD). Electrochemical analyses were performed using a cyclic voltammetry and chrono-techniques.

The amount of Au and Pt in the catalysts was evaluated by ICP-OES and equal to 0.105 and 0.147 mg cm^{-2}, respectively. The electrochemically active surface area of Au and Pt nanoparticles was calculated from the cyclic voltammograms recorded on the investigated catalysts and was equal to 0.23 and 1.1 cm^2, respectively. It has been determined that the $AuCo_3O_4/C$ catalyst showed 3, 8 and 5 times higher electrocatalytic activity towards methanol, ethanol and ethylene glycol oxidation compared with that obtained for the $PtCo_3O_4/C$ catalyst. The $AuCo_3O_4/C$ and $PtCo_3O_4/C$ catalysts also showed an enhanced electrocatalytic activity towards the oxidation of all investigated alcohols compared with the bare Au/C and Pt/C catalysts and Co_3O_4/C substrate.

Investigation of Electrochromism Process through Ultrafast Broadband Spectroelectrochemistry

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Electrochromism is the reversible change in optical properties such as absorbance and transmittance of an electroactive material as a result of an induced redox reaction [1]. Electrochromic materials have gained much research attention since the discovery of organic conducting polymers with high prospects for diverse applications. The redox reaction leading to a color change in electrochromic materials is accompanied by doping/dedoping steps. Considering the oxidation of a neutral conducting polymer (for simplicity), first, the polymer loses electrons in a heterogeneous electron transfer leading to net positive charge creation. To achieve further oxidation, electroneutrality is restored by anions that diffuse from the bulk solution into the polymer. Since the diffusion rate of counterions is much slower than electron transfer, it is widely assumed that the oxidation process is limited by ion transport [2].

To test this assumption we employ Ultrafast Cyclic Voltammetry and broadband UV-visible spectroscopy to decouple ionic charge transfer from heterogeneous electron transfer during electrochromism in poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) thin films. We will present cyclic voltammetric experimental results at sweep rates up to 50kV/s obtained with a home-built fast potentiostat equipped with IR compensation. At such high sweep rates, the period for a full voltage sweep is reduced to the order of microseconds in which counterions do not have enough time to diffuse into the diffusion layer and we effectively exclude their contribution towards electrochromism in the PEDOT:PSS films. At these fast sweep rates, we monitor the electrochromic behavior of the polymer by in situ UV-visible spectroscopy. The collected spectra are compound or averaged spectra (because the spectrometer cannot keep up with the rate of conversion between the redox forms of the polymer during Ultrafast Cyclic Voltammetry). Using principal component analysis algorithm, we will decompose the compound spectra and calculate the time the polymer spends in each of its redox forms during the Ultrafast Cyclic Voltammetric experiments. We will also present the dependence of absorbance of the PEDOT:PSS thin films on sweep rate.

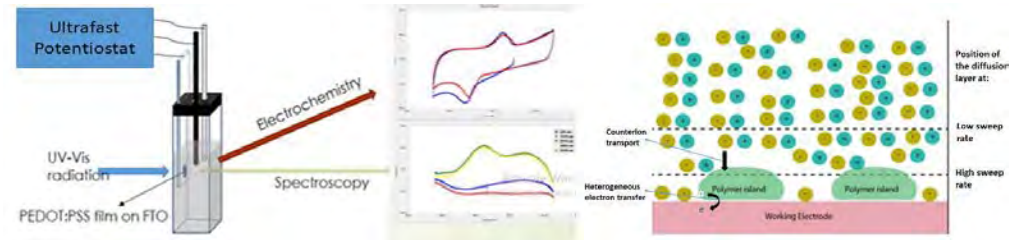

Fig 1. a) Spectroelectrochemistry setup b) Effect of sweep rate on diffusion layer thickness.

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Screening Metal-free Carbon-based Electrodes for the Electrochemical Reduction of CO_2

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In a world that urgently needs to redress the balance of energy derived from fossil fuels, an efficient transformation of CO_2 into valuable chemicals (e.g., formic acid, methanol, methane) has become the key towards combatting climate change, environmental pollution and natural resource challenges. However, being a thermodynamically stable molecule, the ideal concept of a direct conversion of CO_2 into chemical energy has to overcome several limitations such as kinetic barriers to lower overpotentials, increase faradaic efficiency and promote products selectivity [1,2]. As such, its conversion into added value chemical feedstocks and fuels demands highly efficient catalysts. Noble metals are among the most performing catalysts, although they face challenges related to a high cost, sustainability and scarcity of precious metals. For this reason, the research in metal-free catalysts as sustainable and low-cost alternatives is attracting many efforts; advances in the development of highly performing non-metallic catalysts can make possible to overtake metal-based catalysts in the race towards the technological marketplace of carbon dioxide conversion into chemicals [3].

In this context, the objective of the study is to screen metal-free carbon materials as sustainable and efficient electrocatalysts for the conversion of CO_2 into fuels. Despite some carbon materials have been successfully used for this purpose, yet the origin of their electrocatalytic activity and/or the nature of the active sites capable of reacting with the CO_2 molecule remain unclear. Thus a smart design of carbon-based catalysts with adequate electroactive sites is needed**.** For this reason, we have selected a series of carbons with different chemical, structural and textural properties, and analyzed their response as electrocatalysts for the reduction of carbon dioxide under different polarization conditions. A detailed rationalization of the conversion yields and selectivity towards different products will be discussed considering the interactions CO_2-carbon material, analyzing the effect of the pore confinement, the presence of specific surface bonds that might control charge transfer reactions and/or electrochemical features necessary to activate a stable electrocatalytic transformation of carbon dioxide.

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Comparative Study of the Electrical Conductivity of Carbon Materials Measured Using Various Approaches

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Carbon-based electrodes are largely used in many electrochemical applications over a wide variety of competitors owing to the diversity of existing carbon materials with good chemical and mechanical stability, relatively high electronic conductivity, and low cost and sustainability [1-3]. Although some carbons present electronic properties close to those of metallic electrodes (e.g., graphite, graphene and derivatives), this is not the case for many other members of the carbon family, since the heir conductivity depends strongly on the spatial arrangement of the carbon atoms. One example is the case of nanoporous carbons which usually display a low structural order, as a result of which their electronic conductivity is about 4-5 orders of magnitude lower than that of graphite or graphene [4]. For such materials, measuring the electrical conductivity is complex, and despite various methods have been reported in the literature, the comparison of the values obtained by different authors is not straightforward [5,6]. Considering this, the objective of this study was to determine the electrical conductivity of a selection of carbon materials with different structural order, chemical composition, and porous features using various methodologies: four-point probe technique, impedance spectroscopy, Van der Pauw method. Gathered data has shown that the dispersion in the conductivity values is quite low when the carbons display high electron mobility (e.g., graphite, graphene, carbon black). In contrasts, when carbons with moderate to low electron mobility are measured (e.g., amorphous and functionalized porous carbons, graphene oxide, reduced graphene oxide), the differences between the values obtained with different methods become more pronounced. The values obtained using the four probe methods are reliable for carbon materials with a low level of anisotropy, provided that the pellets are homogenous at a macroscopic scale. In contrast, the values obtained by impedance spectroscopy of thin pellets seemed to be quite consistent in all cases.

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Synthesis of ZnO nanostructures in different ethanol containing electrolytes for hydrogen production

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Zinc oxide (ZnO) is a n-type semiconductor with numerous applications in photocatalysis due to its abundance, non-toxicity, versatility and unique photoelectrical properties, as a wide band gap of 3.37 eV and high electron mobility, from 10 to 100 times higher compared to titanium dioxide.

In the present study, ZnO nanostructures were synthesized by anodization method in an aqueous bicarbonate electrolyte with different amounts (10, 25 and 50 v/v %) of ethanol (E) under controlled hydrodynamic (H) and stagnant (S) conditions followed by thermal annealing. Morphology, crystallinity, and vibrational properties of the samples were studied by means of Field Emission Scanning Electron Microscopy (FE-SEM) and Confocal Laser-Raman Spectroscopy. Finally, photoelectrochemical water splitting measurements using ZnO nanostructures as photoanodes were performed.

According to the results, the synthesized ZnO nanostructures presented high photosensibility during water splitting experiments in aqueous Na_2S/Na_2SO_3 electrolyte as it is shown in Figure 1. In particular, the sample anodized in 10 v/v % ethanol electrolyte at stagnant conditions (S-E-10 in Figure 1 (a)) presented the highest photocurrent density response with a value of 0.34 mA/cm^2 at an applied potential of -0.46 $V_{Ag/AgCl}$.

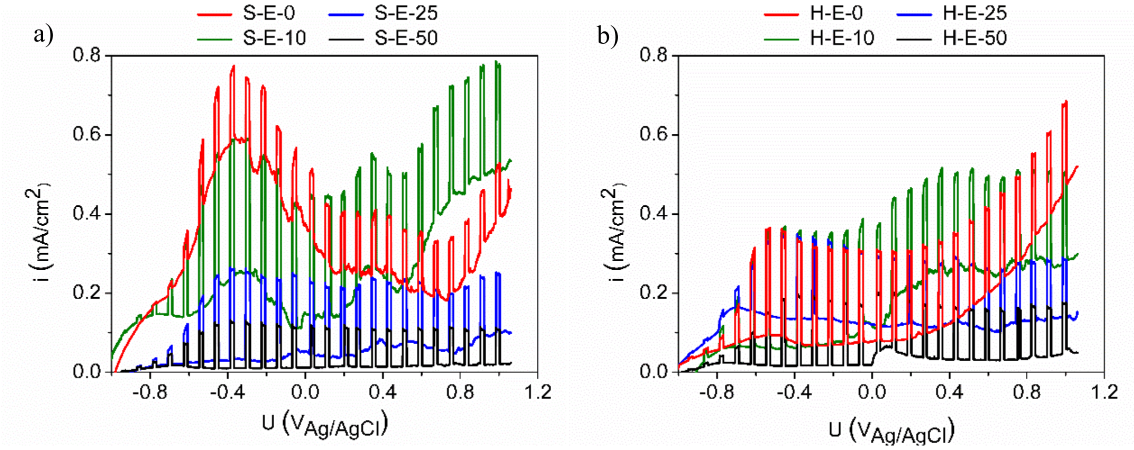

Figure 1. Current density under on/off simulated sunlight as a function of the applied potential for the nanostructures anodized at stagnant (a) and hydrodynamic (b) conditions.

Acknowledgements

Authors thank MINECO (CTQ2016-79203-R) for the financial support and, as well, to E3TECH under project CTQ2017-90659-REDT (MINECO, Spain). Authors would also like to thank the Ministerio de Ciencia, Innovación y Universidades (Project Code: CTQ2017-90659-REDT). R. M. Fernández-Domene also thanks the UPV for the concession of a postdoctoral grant (PAID-10-17). Finally, project co funded by FEDER operational programme 2014-2020 of Comunitat Valenciana (IDIFEDER/18/044) is acknowledged.

Use of WO_3 nanowires for fenamiphos photoelectrochemical degradation

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Wastewater usually contains a large amount of recalcitrant pollutants and its composition is complex. The wastewater pollutants include textile dyes, pharmaceuticals, pesticides, heavy metals, pulp and paper, surfactants, and other chemicals. Therefore, it is crucial to apply clean, environmentally friendly, and efficient wastewater treatment technologies that can remove these pollutants.

Nanostructures of different materials are interesting for being used as photocatalysts in advanced oxidation processes like the one known as photoelectrocatalysis (PEC). Tungsten oxide is one of the best options due to its properties, such as suitable band gap, non-toxicity, high chemical stability in low pH values and ability to absorb a reasonable fraction of the solar spectrum.

In this work, the synthesis of WO_3 nanostructures by electrochemical anodization has been optimized by means of an experiment design 3^3 in which three factors of the process have been varied with three different levels. These factors have been the electrolyte used during anodization, the annealing temperature and the annealing atmosphere in the post-anodization thermal process. The acids used as electrolyte have been sulfuric acid (H_2SO_4), methanesulfonic acid (CH_4O_3S) and nitric acid (HNO_3). The heating temperature varied between 400 °C, 500 °C and 600 °C, while the atmospheres tested were air, nitrogen and argon.

In order to analyze the properties of each sample obtained, different morphological, structural, electrochemical and photoelectrochemical techniques were used to characterize the nanostructures.

Once the optimal nanostructures were obtained, they were used to degrade fenamiphos, a harmful and toxic organophosphate pesticide. For this purpose, the technique known as photoelectrocatalysis was used, where the nanostructures obtained previously acted as photoanodes. This process was monitored using UV-Visible and HPLC to verify that the entire process was going as expected and to subsequently analyze the percentage and kinetics of degradation.

The obtained results showed that the optimal conditions for the synthesis of nanostructures are as follows: use of CH_4O_3S and subsequently heat the nanostructures in an air atmosphere at 600 °C, since a better photoelectrochemical behaviour was obtained. The fenamiphos degradation was achieved at 2 h of experiment and the intermediate formation was noticed at 1 h of PEC experiment.

Acknowledgments

Authors thank MINECO (CTQ2016-79203-R) for the financial support and, as well, to E3TECH under project CTQ2017-90659-REDT (MINECO, Spain). Authors would also like to thank the Ministerio de Ciencia, Innovación y Universidades (Project Code: CTQ2017-90659-REDT). R. M. Fernández-Domene also thanks the UPV for the concession of a postdoctoral grant (PAID-10-17) and G. Roselló-Márquez also thanks the Generalitat Valenciana for the concession of a pre-doctoral grant (ACIF/2018/159). Finally, project co funded by FEDER operational programme 2014-2020 of Comunitat Valenciana (IDIFEDER/18/044) is acknowledged.

Synergic Effects between Carbon and Redox Couples Dispersed in Electrolytes for Zn-air Batteries

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The use of nanocarbons as dispersed conducting particles can bring interesting advantages in the electrolyte of electrochemical storage devices as this material can ensure a high conductivity and area. Moreover, the introduction of multiredox couples dispersed in the electrolyte can also lead to remarkable improvements, as seen in Li/air batteries[1], [2]. These redox couples can act both as redox mediators and catalysts for the oxygen reduction or evolution reactions (ORR, OER) that take place during the battery cycling. Polyoxometalate clusters or other nanoparticles such as IrOx are already known by their catalytic activity in O_2 reduction and reoxidation processes[3].
Herein, the influence of carbon and redox couples in aqueous alkaline and organic media has been studied for Zn-O_2 cell electrolytes. Furthermore, the interaction between carbons and the redox compounds have also been tested, as a significantly enhanced catalytic activity is expected being the redox particles coupled to the carbons. We do observe a synergy between the redox and the conducting species giving rise to enhanced currents and lower overpotentials. The relevant parameters and hypothesis for a mechanism will be discussed.

Acknowledgements

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Nitrogen-doped Nanoarrays Modified 3D Hierarchical Graphene as Co-Function Host for High Performance Flexible Li-S Battery

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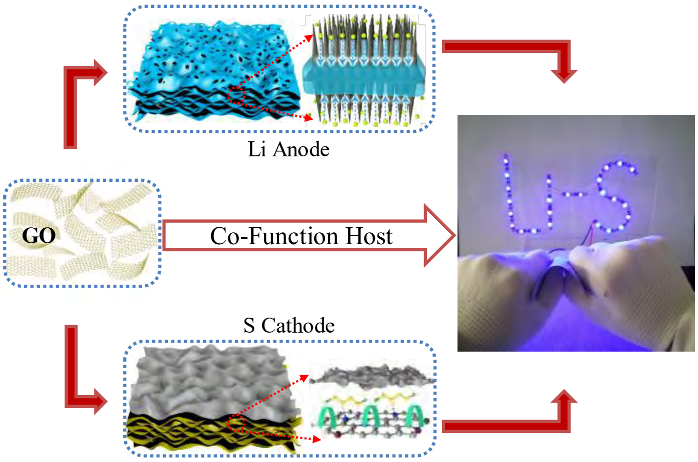
Lithium-sulfur (Li-S) batteries with high energy density and low cost are regarded as promising candidates for the next-generation energy storage systems.[1] Practical application of Li-S batteries is still hindered by both the shuttle effect of polysulfides and the severe Li dendrites growth. To overcome challenges in Li-S batteries, various ways have been thoroughly explored for Li anode or S cathode separately with little attention to the co-function hosts for both Li and S.[2, 3] We believe that the co-function hosts are prospective with simultaneous promotion for both Li anode and S cathode. Luckily, there are various similarities in the design of structures and properties, such as highly conductive skeleton to effectively host active materials and uniformly polar surface to improve the performances, which makes it possible to use the same material to improve performances simultaneously. Therefore, to build an approach of co-function hosts for Li anode and S cathode simultaneously, a rational design of 3D hierarchical skeleton is highly desired.

Herein, we designed and fabricated a 3D, freestanding and hierarchical porous reduced graphene oxide with N-doped nanoarrays (3DRGO/NC) as the co-function host for Li anode and S cathode. The 3D freestanding porous RGO forms the main skeleton structure to hold the Li metal and elemental S, and heteroatom N doping can lower the Li nucleation overpotential and immobilize the polysulfides. More importantly, the well-aligned nanoarrays can effectively confine Li-ions flux and provide an optimized ion-diffusion pathway for better Li plating/stripping behavior and enhanced S utilization/conversion. Particularly, an ultrathin graphene barrier layer was built on RGO with N-doped nanoarrays (3DRGO/NC-BL) which can effectively retain intermediate polysulfides staying in the cathode through physical confinement. As a result, the 3DRGO/NC shows a perfect Li plating behavior without growth of Li dendrite or "bulk" Li deposition, high CE of 98.0% for 300 cycles with low nucleation overpotential (14 mV), long cycle lifespan (500 h) and perfect rate performance. The 3DRGO/NC-BL exhibit high initial discharge capacity of 1185 mAh g^{-1} with excellent CE and present a long stability up to 500 cycles with high-reversible specific capacity of 927 mAh g^{-1}. Most importantly, a flexible battery is demonstrated with excellent performance in flat, bent, and even rolled states by combining 3DRGO/NC@Li anode and 3DRGO/NC-BL@S cathode, which provide a promising strategy for flexible energy-storage devices.



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Surface modification of electroactive materials particles with titanium carbosilicide: structural and electrochemical study

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The compounds of the so-called MAX phases class (where M is a transition metal, A is an element of the main subgroup of the III-V groups of the periodic system, X is carbon or nitrogen), which were firstly synthesized in the 1970s are widely used as the basis of structural materials due to high mechanical strength, outstanding heat and electroconductive properties, as well as chemical stability [1]. We used one of such compounds – Ti_3SiC_2 (TSC) [2] for the particles surface modification of polyanionic cathode materials for lithium-ion battery e.g. $Li_3V_2(PO_4)_3$/carbon composite (LVP/C). TSC modified LVP/C demonstrates improved electrochemical behavior (Fig. 1) [3].

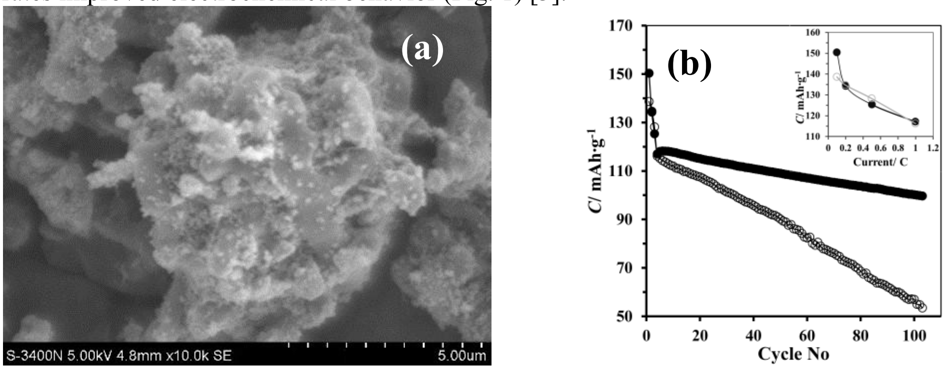

Fig. 1: Scanning electron micrograph (*a*) and galvanostatic charge/discharge capacity behavior (*b*) of the TSC-modified LVP/C-electrode. Empty markers of (b) correspond to the material with bare particles, filled markers – TSC-modified particles.

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Modified Blue Algae Biochar Electrode for CO2RR

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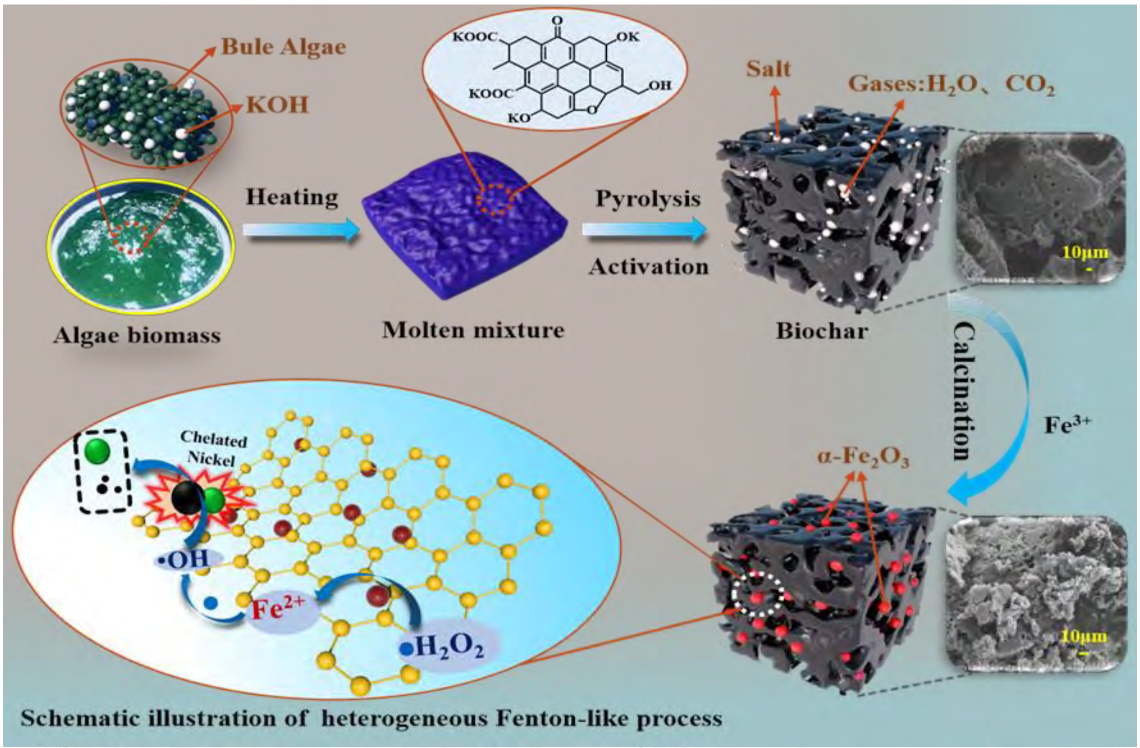
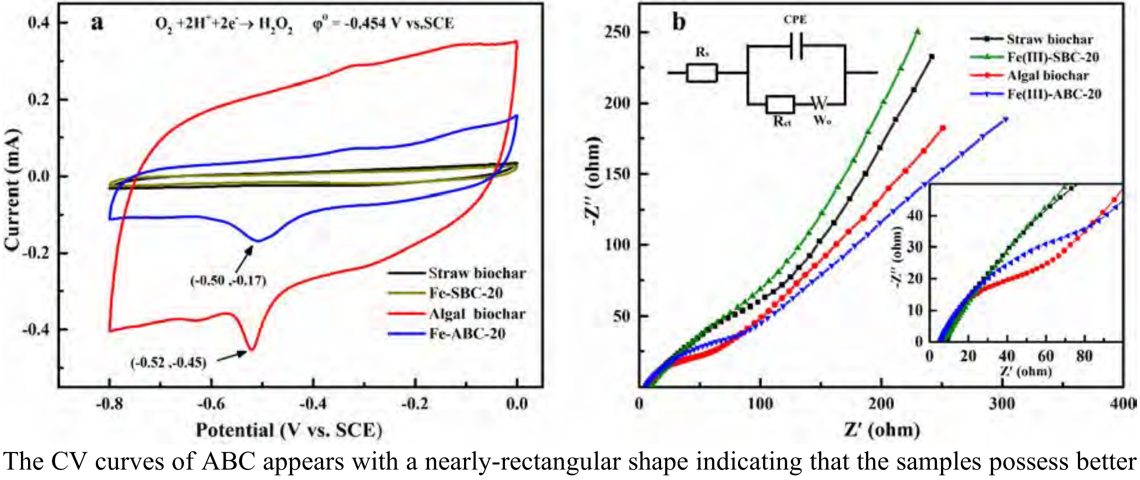


Schematic illustration of heterogeneous Fenton-like process



The CV curves of ABC appears with a nearly-rectangular shape indicating that the samples possess better capacitance traits and smaller internal resistance. After the iron loading, the CV curve is significantly narrowed and the current peak shifts to -0.5 V. This is due to the iron loading blocked the porous algal biochar structure, thereby reducing the electric double layer capacitance. In addition, the right shifting and widening of the current peak could be attributed to the reduction of Fe(III) via the presence of ligand to metal charge transfer (LMCT).

EIS curve of the ABC electrode appeared as an approximate semicircular arc with smaller diameter than that of Fe(III)-ABC-20, SBC and Fe(III)-SBC-20 electrodes, implying the ABC based electrode possess lower electron transfer resistance than their SBC based counterparts.

Nitrogen-doped graphenic materials: towards platinum-free catalytic layers in PEMFCs

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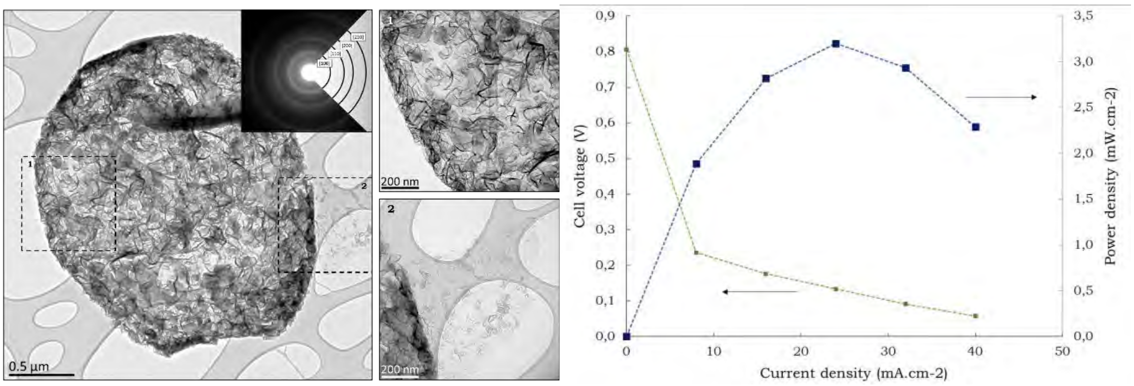
Platinum nanoparticles dispersed over porous carbon materials are still widely used as catalysts for oxygen reduction reaction in polymer fuel cells. However, platinum resources are diminishing rapidly, and the lack of recycling solution will aggravate the situation for this critical metal during the next century. Nitrogen-doped graphenic materials are investigated as cheap alternative to platinum since nitrogen is able to catalyze oxygen reduction by partially redistributing the electric charges of the neighboring carbon atoms.

An original synthesis route to nitrogen-doped graphenic foam has been developed, this material exhibiting both polycrystallinity with surface area up to 2200 $m^2.g^{-1}$, and electrochemical properties brought by the nitrogen doping (1-3 at.%).

Recently, our materials have been tested in a complete PEMFC setup in impedance and potentiometric measurements, to assess their performance in energy production and their kinetic capacities. First tests showed that N-doped graphenic foam as cathode catalyst, allows current density over 30 $mA.cm^{-2}$, a power density of 3.2 $mW.cm^{-2}$, approximately 50-fold larger than with nitrogen-free graphenic foam. While nitrogen atoms appear essential to catalytic activity, intrinsic carbon defects nature, pore size or oxygen functions content could also play an essential role for catalysis purpose, as currently studied to optimize furthermore our materials.



TEM micrographs of N-doped graphenic foam; electrochemical performance of N-doped graphenic foam as cathode catalyst during PEMFC operation

Photoremoval of Cyanobacteria and Cyanotoxins by Magnetic ZnO-based Photocatalysts

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Promoted by rising global temperatures and anthropological trends such as water pollution, the formation of harmful cyanobacterial algal blooms and, in turn, the release of cyanotoxins are becoming major problems worldwide. In response, the development of efficient, effective strategies and technologies for treating cyanobacteria and cyanotoxins, especially in drinking and recreational water, is urgently required. In the study reported here, a circular process (**Figure 1**) for water decontamination and biofuel production to minimize the generation of residues and improve the efficiency of photocatalysts was proposed. Spirulina was cultivated using microalgal ashes while carbon dioxide was fixed and oxygen was released, and microalgal ashes generated during the combustion of microalgal pellets were recycled as a supplement for the cultivation media. Next, magnetic hybrid ZnO-based photocatalysts were synthesized following a biotemplating process involving Ni electroless deposition, ZnO deposition, and sulfidation, which led to the formation of onion-shape Ni@ZnO@ZnS-microalgae hybrids. Ultimately, the hybrids, which exhibited excellent photocatalytic activity for the degradation of cyanotoxins (i.e., anatoxin-A) and two species of cyanobacteria, were implemented for water decontamination using sunlight irradiation and recycled after their effective lifetime for the manufacture of microalgal biopellets as biofuel.

Figure 1: Schematic representation from reference [1].

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Green Electrosynthesis of 4-Aminophenol by using Electrodeposited Porous Au Micropillars

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Using 4-aminophenol as an intermediate in manufacturing analgesic and antipyretic drugs has given the product important commercial value. Currently, several methods are available for synthesizing 4-nitrophenol, the most relevant being the multistep iron-acid reduction of 4-nitrochlorobenzene or 4-nitrophenol, the catalytic hydrogenation of nitrobenzene, and the electrochemical reduction of 4-nitrophenol. However, the necessary use of highly corrosive mineral acids and dangerous toxic reducing agents, poor chemoselectivity and yields, and the growing demand for 4-aminophenol demonstrate the need for developing or optimizing green, efficient routes for preparing 4-aminophenol. Among possible options, organic electrosynthesis can realize an environmentally friendly, chemoselective redox transformation under conditions free of exogenous reductants due to the use of electric current. However, the optimization of efficient electrocatalysers and electrochemical media conditions needs to be further studied to propose such a route for synthesizing 4-aminophenol.

In the study reported here, the electrosynthesis of highly accessible, well-defined porous Au micropillars for use as electrocatalyzers in the chemoselective electroreduction of 4-nitrophenol was optimized. Using the double shape-controlled electrodeposition of Au based on the combination of 3D laser lithography and colloidal lithography allowed the reproducible synthesis of porous Au micropillars with highly accessible surface areas. Additionally, using the porous Au micropillars in moderately acidic conditions realized the electrosynthesis of 4-aminophenol, both in high yields and with high chemoselectivity. Porous Au micropillars can thus also contribute to an efficient, environmentally friendly method of removing 4-nitrophenol from wastewater. The electrosynthesis of porous Au micropillars as electrocatalyzers for 4-nitrophenol reductions can offer a competitive, ecofriendly strategy for electrosynthesizing 4-aminophenol and decontaminating wastewater.

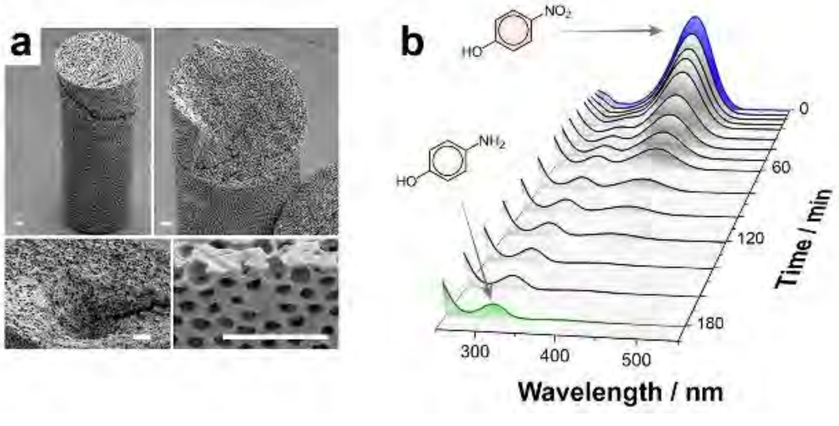

Figure 1: (a) FE-SEM micrographs. Scale bar: 2 µm. (b) Time-dependent UV-vis spectra at 20 °C.

Acknowledgment
Albert Serrà would like to acknowledge funding from the EMPAPOSTDOCS-II program (Marie Sk1odowska-Curie grant agreement number 754364).

Investigation on the Photoconductivity of Covalently Grafted None-noble Metal Polyoxometalates-porphyrin Copolymer

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Polyoxometalates (POMs) are composed of cations and polyanion clusters with structural diversity. POM anions in their ground states can be excited by UV or near- visible light.[1, 2] The essence of excitation is the charge transfer from an oxygen atom to the d^0 TM (transition metal) in the presence of light with abundant energy. In order to expand its application scope, we expect it to be connected with porphyrins, a common photosensitizer, and applied to the visible region.[3] Here, a non-noble Fe-based POM (Anderson) with ZnT_2P porphyrin was synthesized by electropolymerization. This process was also monitored by EQCM (Electrochemical Quartz Crystal Microbalance). The copolymer was characterized by UV-Vis-NIR spectroscopy, electrochemistry.

Their electrical properties have been studied by electrochemical impedance spectroscopy and their photovoltaic performances have been investigated by photocurrent transient measurements under visible-NIR light irradiation. The photocurrent for the $Fe^{III}POM\text{-}ZnT_2isoP^{\bullet}$ copolymer can be up to 200 μA/cm^2.

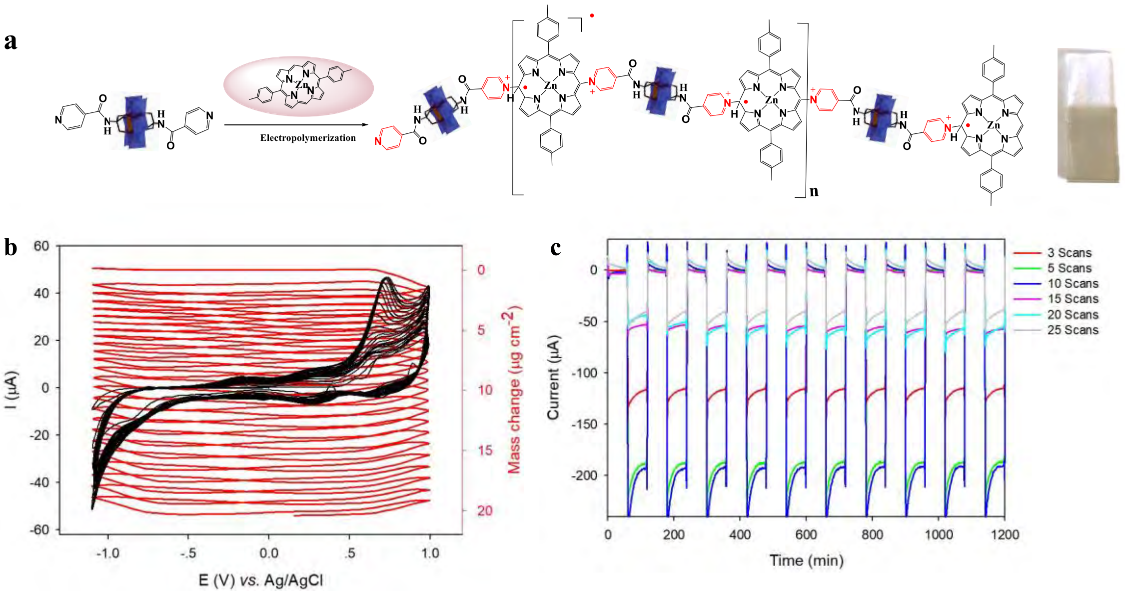

Figure 1. a) Structure of $Fe^{III}POM\text{-}ZnT_2isoP^{\bullet}$ copolymer. **b)** Consecutive cyclic voltammograms (first 25 scans) and electrochemical quartz crystal microbalance measurements (Δm) for the first 25 scans during the electropolymerization. **c)** Transient photocurrent study for $Fe^{III}POM\text{-}ZnT_2isoP^{\bullet}$ copolymer.

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Versatile Decoration of Carbon Support with Metal Nanoparticles for Electrocatalytic Application

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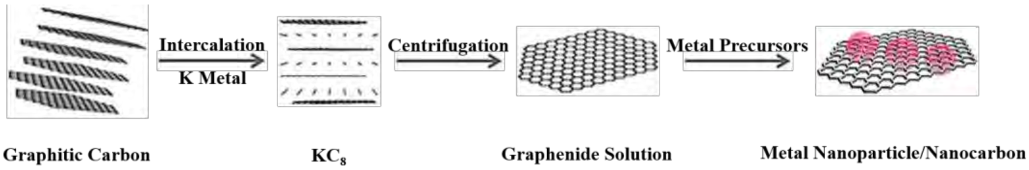
The development of efficient catalysts is significant in order to achieve the shift from fossil fuels to sustainable alternatives, such as hydrogen energy.[1] One of the promising ways to synthesize electrocatalysts is to combine metal nanostructures with supports that possess high electrical conductivity as well as high surface area.[2,3] Here, we reported a general method for the synthesis of metal nanoparticle/nanocarbon composite, denoted as M(nP)/nC, which included generation of graphenide solution from graphitic carbon source and reaction between graphenide solution and metal salt. Electrocatalytic performance of the prepared materials were measured for reactions in water electrolyzer and fuel cell, such as the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR).

On the one hand, starting with various carbon sources, graphenide solutions with carbon flakes differing in lateral dimension were achieved; after reaction with iron salt, iron nanoparticle/nanocarbon composites were generated with controllable size of iron nanoparticles. Electrochemical measurements showed that the choice of initial carbon was crucial for determining the scale of carbon flake and simultaneously tailoring the size of iron nanoparticles, which had a major impact on electrocatalytic performance for the ORR and OER. On the other hand, following the same synthetic method, when tuning metal species from transition metal iron to noble metal rhodium, nanocarbon with decoration of rhodium nanoparticles was also successfully synthesized and displayed efficient electrocatalytic activity for the OER and HER in alkaline condition.



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Enhancing the Catalytic Activity of Pd Nanoparticles for the Ethanol Oxidation Reaction in Alkaline Media by Developing a Vulcan Support Functionalized with the Mesityl Cu Organometallic Compound

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Herein, Vulcan XC-72 was functionalized with the home-obtained mesityl copper (Cu-mes) organometallic compound. $C_{Cu\text{-}mes}$ was characterized by FTIR, and Raman. The results showed the successful incorporation of organometallic compound and structural modification of Vulcan. Afterwards, Pd nanoparticles were dispersed on the novel supports by the polyol method, obtaining 20 wt. % $Pd/C_{Cu\text{-}mes}$. The nanocatalyst was characterized by XRD, where a shift towards higher 2θ angles indicated the formation of alloyed Pd-Cu phases. The crystallite size was estimated using the Scherrer equation, obtaining values of 2.9 and 6.9 nm for $Pd/C_{Cu\text{-}mes}$ and conventional Pd/C, respectively. Chemical composition analysis showed that the organometallic compounds are chemically stable, maintaining a high Cu concentration after the synthesis of the nanocatalyst. XPS analysis of $Pd/C_{Cu\text{-}mes}$ indicated mainly the presence of Cu^0 and Cu^{+2} in the Cu 2p region. At the Pd 3d region, the Pd^0, Pd^{+2}, Pd^{+4} species have been identified. In the case of Pd/C the three species were also observed. Moreover, there was a shift to higher BE of the doublets in $Pd/C_{Cu\text{-}mes}$ compared Pd/C, attributed to the chemical interaction between Pd and Cu. The electrochemical characterization was performed in 0.5 mol L^{-1} KOH. The ECSA values of $Pd/C_{Cu\text{-}mes}$ and Pd/C were 118.72 and 24.55 $m^2\ g^{-1}$, respectively. A higher value was obtained for $Pd/C_{Cu\text{-}mes}$, indicating a large number of active sites that participate in the electrochemical reaction, which can also be related to the electrocatalytic activity of the nanocatalyst. The catalytic activity of the nanocatalyst in CO-stripping tests showed that the CO oxidation occurs at more negative potentials in $Pd/C_{Cu\text{-}mes}$ compared to Pd/C. The polarization curves of the EOR at the nanocatalysts showed that $Pd/C_{Cu\text{-}mes}$ promotes the reaction at a more negative onset potential, i.e., E_{onset} = 0.38 V/RHE, compared to 0.41 V/RHE of Pd/C. The mass current density (j_m) was considerably higher at $Pd/C_{Cu\text{-}mes}$ (1234 mA $mg^{-1}{}_{Pd}$), compared with Pd/C (665 mA $mg^{-1}{}_{Pd}$). An electrolysis test was carried out for 4 h where is important to remark that the nanocatalysts supported in functionalized Vulcan consumed a higher percentage of ethanol (61%) during electrolysis than Pd/C (47%), which indicated a higher catalytic activity and stability over time. In AEM-DEFC tests, the cell equipped with a $Pd/C_{Cu\text{-}mes}$ nanocatalyst anode showed the highest open circuit voltage (OCV) 0.60 V, compared to 0.50 V at the cell having a Pd/C anode, respectively. The maximum power density value was 0.14 W cm^{-2} at 0.5 A cm^{-2} by $Pd/C_{Cu\text{-}mes}$. The results of this study clearly showed an enhanced behavior for the EOR in alkaline media by the nanocatalysts supported on functionalized Vulcan with Cu-mes, attributed to the formation of alloy phases between Pd and Cu and therefore the combination of the bifunctional mechanism, as well as ligand and strain effects. In summary, $Pd/C_{Cu\text{-}mes}$ showed a high catalytic activity in AEM-DEFC applications.

Electrochemical Investigation of Gramicidin Reconstituted into Liquid Crystalline Cubic Phases

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Liquid crystalline phases composed of lipids, water and incorporated ionophores such as gramicidin, provide a useful tool for the study of membrane transport. Lipidic cubic phase (LCP) consists of interpenetrating but noncontacting aqueous channels surrounded by a lipid bilayer. These compartments are continuous in three dimensions, so the mesophase is called "bicontinuous". Specific features of lipid cubic phase structure make them convenient for electrochemical measurements: they are stable in the presence of excess of water, highly viscous, and can be easily placed at the electrode surface. The amount of protein sample needed for the measurements is small and its stability is increased. Such membrane is biomimetic and the conditions resemble those typical for biological bilayers - therefore the incorporated proteins and peptides can maintain their activity.

Gramicidin is a polypeptide antibiotic, a dimer that forms small pores in the membrane and allows the movement of monovalent cations. The antibacterial effect of gramicidin is based on increasing the permeability of e.g. potassium ions through membranes, which ultimately leads to the death of the bacterial cell. In the literature there are other examples of the pore forming peptides applied as drugs[1] and a number of studies on diseases in which the formation of pores occurs in the cell membrane including bacterial infections[2] or Alzheimer's disease[3]. Gramicidin, due to its small size and easy accessibility, can serve as a good model of transmembrane channels.

The goals of our study were to prepare a stable monoolein cubic phase (*Pn3m*) with and without incorporated gramicidin. The phase identity and structural parameters of the lipid samples were determined by Small-Angle X-ray Scattering (SAXS). The ion transport of gramicidin incorporated into LCP was studied by cyclic voltammetry (CV) and chronoamperometry (CA). The glassy carbon electrodes covered with a film of cubic phase with and without gramicidin were exposed to solutions of different concentrations of KCl and the currents were recorded upon application of potential steps towards positive and negative values of potential. The electrode capacitance and resistance of the films were evaluated by impedance spectroscopy (EIS).

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Disulfide Bridges-based Polymer as Cathode for Rechargeable Li and Mg Batteries

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The new technological era to take over from Li battery system is currently investigated at a fast rate.[1] In this regard, the Mg based battery system has gained considerable popularity as an alternative system since they proffer to provide one of the best economical solutions for electrical storage.[2,3] Contrary to metal-based inorganic active materials, organic materials seem very well adapted to the divalent character of Mg^{2+}, and the performance obtained with Mg^{2+} opening a wide window of investigations for the development of organic positive electrodes with high capacity using Mg as negative electrode. In this study, polybenzoquinonyldisulfide (PBQDS) in lithium and magnesium-based electrolytes were investigated using cavity micro-electrode technic and galvanostatic cyclic tests. In this study, diglyme and sulfolane solvents, associated with both LiTFSI and $Mg(TFSI)_2$ were used. The electrochemical characteristics of PBQDS are truly similar in term of potential and ΔE_{peak} in both lithium and magnesium systems at a relative high scan rate, i.e. 1 mVs^{-1}. An improvement of the redox couple reversibility seems to be observed in Mg form, with a ΔE_{peak}= 400 mV with $E_{1/2}$ near 3 V *vs* Mg^{2+}/Mg. Based on this interesting behavior, PBQDS was investigated in a coin cell configuration as active material in the present of glyme or sulfolane based electrolytes. The cell achieved a stable capacity of 140 $mAh.g^{-1}$ in sulfolane + LiTFSI at C/20, whereas a value of 105 $mAh.g^{-1}$ in sulfolane + $Mg(TFSI)_2$ can be obtained. The electrochemical process involved in both Mg and Li based electrolytes was compared.

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A kinetic study of the chemical interaction between neurotransmitter dopamine and the highly used anti-psychotic drugs olanzapine and quetiapine.

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Mental disorders like schizophrenia affect about 0.7% of the world population[1]. Nowadays, the treatment consists of atypical anti-psychotic drugs, mainly olanzapine (OLZP) and quetiapine (QTP)[2]. It was observed a chemical interaction between both OLZP and QTP ~~, anti-psychotic drugs,~~ with dopamine (DA) in phosphate buffer solutions at physiological pH using cyclic and differential pulse voltammetry techniques. DA electrochemical oxidation was hindering in the presence of both OLZP and QTP. ~~A solution containing both anti-psychotic drugs and DA presented a shift of DA's redox processes, hindering its electrochemical oxidation. We investigate the chemical interaction voltametrically and obtained that b~~Both drugs presented ~~a first~~ first-order kinetics with DA, presenting kinetic rate constants of 1.54 10^{-2} s^{-1} and 7.78 10^{-3} s^{-1} for OLZP and QTP, respectively. To further evaluate the ~~the~~ chemical reaction, a minimalist model ~~between~~ was proposed using PIPES buffer ~~molecule~~ and ~~cathecol~~catechol to simulated the DA- drug interaction. ~~was proposed and tested.~~ The model presented a similar signal decrease and kinetic rate constant with those observed for both OLZP and QTP reaction with DA, suggesting that a chemical interaction occurs between piperazine and catechol moieties.

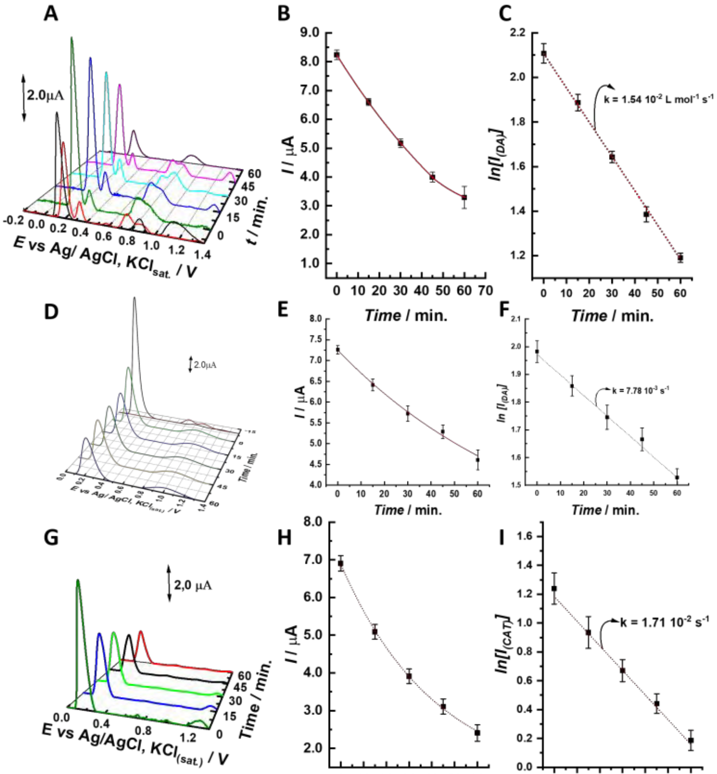

Figure 1: DPV of solutions containing A) 1.0 mM, each, of OLZP and DA; D) 1.0 mM, each, of QTP and DA; G) 1.0 mM, each, of Pipes and CAT in PBS 0.1 M, pH = 7.4; I x t plots of the respective DPV (B-A; E-D; H-G); lnI x t plots of the respective DPV (C-A; F-D; I-G).

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PEDOT Nanotubes: From Synthesis to Energy Storage and Electrocatalysis Applications

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Nanostructured conducting polymers have been extensively studied to improve properties and achieve new characteristics when compared to bulk polymers. In this work, poly-3,4(ethylenedioxythiophene) nanotubes (PEDOT-NTs) were successfully electrodeposited onto flexible stainless-steel mesh electrodes in the presence of methyl orange (MO) template [1]. It was found that the pH of the reaction medium is an important parameter to tune up the final morphology (Fig. 1). The modified electrodes were characterized by scanning electron microscopy (SEM) and transmission electron microscopy. To better understand the mechanism of nanotube formation, the current-time transients obtained in the synthesis were fitted according to a theoretical model.

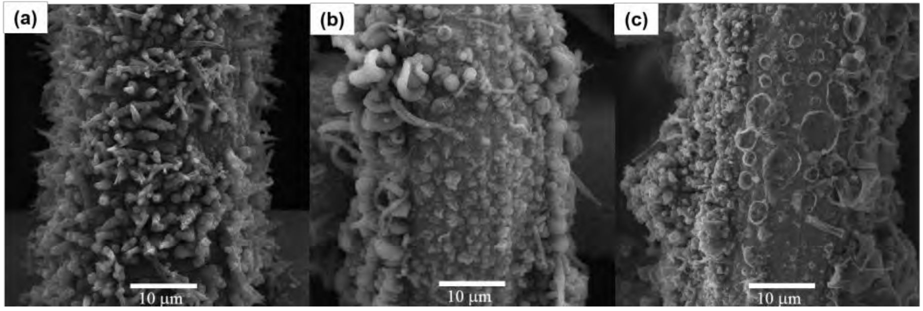

Fig. 1. SEM images of PEDOT synthesized in the presence of MO at (a) pH 2, (b) pH 4 and (c) pH 7

In this work, we report the study of the multifunctionality of PEDOT-NTs synthesized at pH 2 in energy storage and electrocatalytic degradation of nitrophenol isomers. The United States Environmental Protection Agency listed NPhs as priority pollutants, and *ortho* and *para* are classified as hazardous substances [2]. Moreover, nitroaromatics compounds are stable and recalcitrance to degradation [3]. The NPh reactions (Fig. 2(a)) provided an enhanced pseudocapacitance performance, reaching a specific capacitance 50% higher than PEDOT-NTs in the absence of NPhs (Fig. 2(b)). The presence of NPhs during the charge and discharge curves also increased the stability of the material (Fig. 2(c)) by forming poly(aminophenols) during the electrocatalytical processes. The extension of NPh degradation was evaluated by UV-Vis spectroscopy and the electrodes were characterized by electrochemical, vibrational spectroscopic and scanning electron microscopy techniques. By this way, this contribution presents an interesting perspective gathering the degradation of micropollutants and the energy storage devices which are certainly two of the biggest concerns of the scientific community nowadays [4].

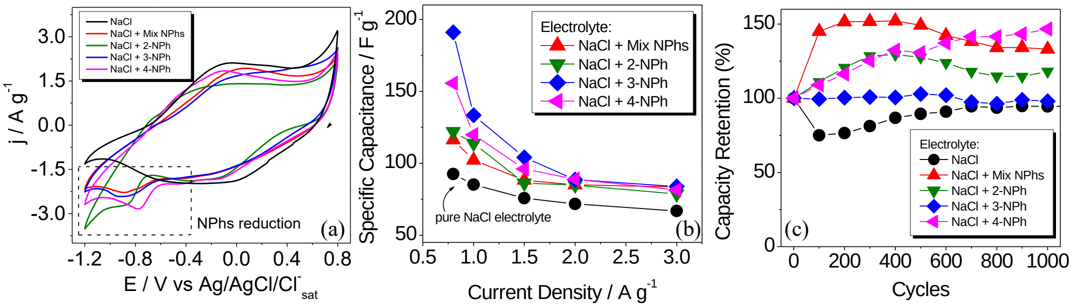

Fig. 2. (a) CVs of PEDOT-NTs at 20 mV s^{-1}, (b) specific capacitances calculated from GCD cycles at different current densities and (c) stability of the modified electrode during 1000 GCD cycles at 3 A g^{-1} in 1 mol L^{-1} NaCl in the absence and in the presence of NPhs.

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Pt Dimers in a Pd Lattice for the Oxygen Reduction Reaction

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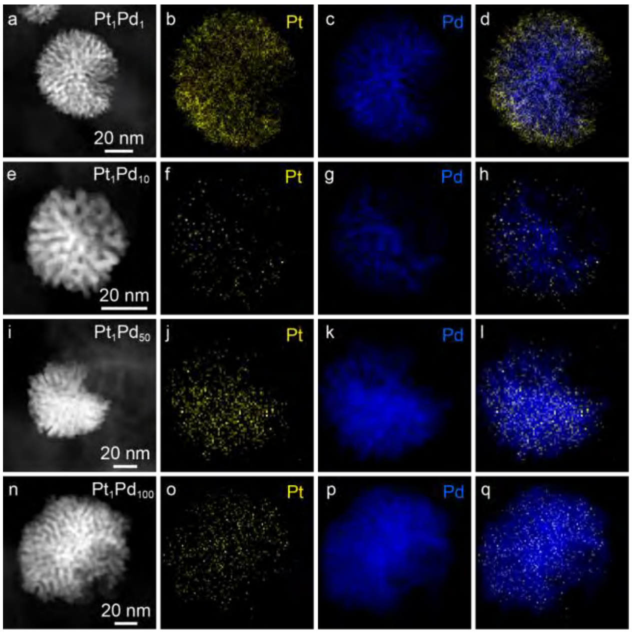
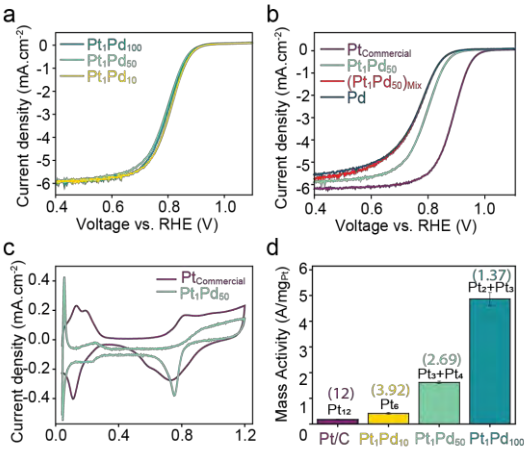
The oxygen reduction reaction (ORR) is widely studied in energy materials as it occurs at the cathode of a hydrogen fuel cell. Materials used currently face two major challenges – the high cost of Pt (reducing or replacing Pt) and the sluggish reaction kinetics (Pt is still the most active material known).

We propose the economical use of Pt in cathode systems by the precise design of atom efficient catalyst materials. Dimers are some of the smallest active centers that dissociate double and even triple bonds (e.g. O_2, NO, CO_2). This is particularly important in the electrochemical ORR where the O=O dissociation and subsequent desorption of oxygen species are crucial in achieving high mass activity. Here we report the design of Pt dimers within a Pd nanoparticle (NP) framework to reach a mass activity of 4.867 $A.mg_{Pt}^{-1}$, 23 times that of commercial Pt/C.





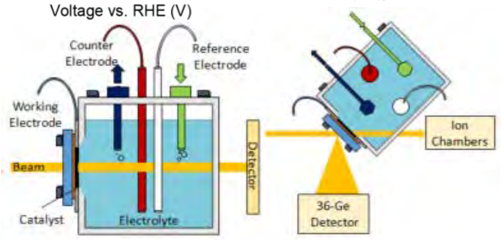


Figure 1(left): 20nm scale transmission electron microscopy (TEM) images of nanoparticles (first column) and energy dispersive spectroscopy (EDS) mapping showing the Pt (yellow), Pd (blue) and combined signal (last column) distribution. Figure 2(top right): (a) Electrochemical results of prepared nanoparticles, (b)comparison of mixture and alloy alongside reference materials, (c)cyclic voltammetry results and (d) exponential relationship observed between mass activity and Pt cluster size.Figure 3(bottom right): In situ electrochemical cell designed to monitor changes in oxidation state.

Pt-Pd NPs were synthesized through co-reduction with Pt:Pd ratios of 1:10, 1:50 and 1:100. Electron microscopy and elemental mapping in **Fig. 1** confirmed the even distribution of Pt on highly porous, flower-like Pd NP frameworks. The catalytic performance of NPs in **Fig. 2** was comparable with commercial Pt/C (**Fig. 2a,b,c**). The alloying effect achieved with colloidal growth increased activity, proven by comparison of an alloy and a physical mixture with the same ratio (Pt1:Pd50), plotted in **Fig. 2b**. It is believed that the Pt dimer absorbs and dissociates O_2, while the neighbouring Pd atoms activate H^+. The Pt cluster size in **Fig. 2d** was extrapolated from extended X-ray absorption fine structure (XAFS) fitting of Pt coordination. Increase in Pt cluster size led to a 60% decrease in the mass activity.

In situ XAFS monitoring found that a bulk sample (Pt1:Pd1) was oxidized during ORR while in extreme ratios (Pt1:Pd50) oxidation state was constant, attributed to Pt stabilization at the surface. The high mass activity achieved and in situ characterization of catalysts during ORR makes this research particularly relevant. We conclude that the precise molecular engineering of well-defined dimers is the key to activating chemically stable compounds, particularly in the utilization of renewable energy.

Design of low potential viologen-modified redox polymers for bioelectrochemical applications

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Bioelectrocatalysis is a promising research field for the development of sustainable energy conversion devices [1] and biosensors. The two main challenges for the development of new devices are the typically low current output due to inefficient wiring of enzymes or slow electron transfer in the matrix, and short lifetimes that can be attributed to the fragility of enzymes or instability of components forming the electrode archi-tecture [2,3].

A widely used strategy to ensure high electron transfer rates is to use redox polymers that electrically connect the redox centres of enzymes to electrodes through redox functions attached to the polymer backbone [4,5]. Possible limitations can be addressed by wiring enzymes in specifically designed redox polymers that are stable, provide a more efficient electron transfer and have an adapted potential to maximize the e.g. the open-circuit voltage of a biofuel cell or a self-powered sensor or to circumvent side reactions due to the co-oxidation/-reduction of interferences.

This work explores the design of tailored viologen-modified redox polymers for efficient wiring of low potential redox proteins, such as e.g. hydrogenases for the use in bioelectrodes. Firstly, the redox potential, determined by the potential of the redox mediator, the stabilizing effect of the polymer matrix [4, 6] and charged functional groups that can change the potential by electrostatic interaction [7], is adjusted with respect to the properties of the enzyme. Secondly, anchoring of viologen units to the polymer backbone needs to ensure both stability of the connection and mobility of polymer segments [5]. Thirdly, the stability and solubility of the polymer is determined by the ratio of hydrophobic and hydrophilic groups and the degree of crosslinking.

Considering these prerequisites, we have synthesized various viologen-modified redox polymers, changing the nature and the ratio between functionalities. Newly synthesized redox polymers have been evaluated for the use in bioelectrodes e.g. by integrating hydrogenases for possible application as bioanodes in biofuel cells [6, 8].

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Stable metallo-isoporphyrin copolymer: electrochemical mechanism and photovoltaic properties

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Isoporphyrin are mainly described in the literature as an intermediate of the reaction (biosynthesis of chlorophyll molecules as well as heme oxidation). The formation of isoporphyrins can be obtained upon nucleophilic attack on oxidized porphyrin. Optical spectrum of isoporphyrin present a typical strong absorption at the near-IR region but also remarkable redox behavior [1]. Most of the isoporphyrin reported show a high tendency to decompose either by ring opening or by rearomatization to give the starting porphyrin [2]. But, different procedures have developed to synthesize stable isoporphyrins [3].

In this presentation, new strategy to obtain stable isoporphyrin integrated in the polymers will be presented and will be compared with "classical" porphyrin copolymer with viologen spacers developed in our group [4]. Electrogenerated radical cation as well as dication porphyrin using porphyrin such as zinc 5,15-ditolyl-porphyrin (**ZnT$_2$P**) are powerful electrophiles which can rapidly react with nucleophiles such as dipyridyl ligand (py-R-py) to form copolymers containing stable isoporphyrins (**poly-ZnT$_2$isoP$^{\bullet}$**) or porphyrin (**poly-ZnT$_2$P**) depending of the applied potential chosen. Mechanisms of electrochemical routes to these electroactive copolymers will be presented as well as the optical and amazing redox properties of poly-**ZnT$_2$P** and **poly-ZnT$_2$isoP$^{\bullet}$** (Fig. 1). Formation of these two copolymers has been monitored by EQCM. The impedance properties (EIS) as well as the photovoltaic performances have been investigated where p**oly-ZnT$_2$isoP$^{\bullet}$** present considerably better performance in comparison of **poly-ZnT$_2$P**. Excitation of this new NIR band for the isoporphyrin radical copolymer lead, in the aerated media (presence of O_2), to the formation of the singlet state of the dioxygen $^1O_2$ which is the first step for the use of such materials for the photodynamic therapy for cancer.

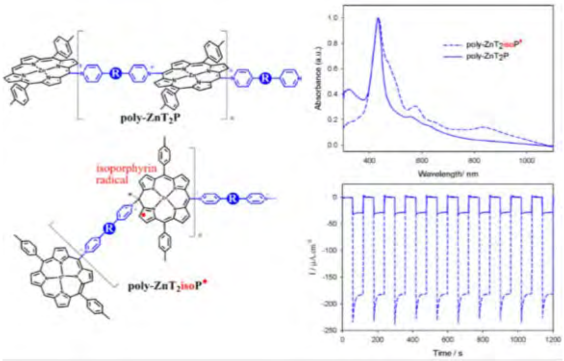

Figure 1. Left: structures of copolymers **poly-ZnT$_2$P** and **poly-ZnT$_2$isoP $^{\bullet}$**. Right: optical and photocurrent characteristics of **poly-ZnT$_2$P** and **poly-ZnT$_2$isoP $^{\bullet}$** copolymers.

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Understanding of the Electrochemical Degradation of Nitrogen-doped Pt/C Electrocatalysts for PEMFC

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Currently, carbon black as support material has been widely used for PEM fuel cells. Degradation of state-of-the-art Pt nanoparticles (NPs) supported on carbon black is based on Ostwald ripening, particle agglomeration, Pt dissolution and/or Pt NP detachment associated with carbon corrosion.[1] The use of functional groups such as nitrogen incorporated in the carbon structure improves the (electro-)chemical stability of the Pt NPs by anchoring sites [2] and corrosion resistance of the support material.[3] However, the (electro-)chemical degradation of different N species during the ORR is still unclear.

In this work, we have combined a synthetic approach to tune the N content incorporated into the carbon material by using pyrolysis of 1,10-phenanthroline and iron(II)-acetate[4] with a deposition of platinum NPs (20 wt.-%) *via* wet-impregnation technique. Based on comprehensive XPS analysis, the N-doped carbon contains pyridinic (48%), pyrrolic (41%) and graphitic (11%) N surface species giving a total N content of 2 at.-%. The as-prepared N-doped Pt/C shows similar mass activity ($i_{mass}=0.23 \pm 0.07$ A mg^{-1}_{Pt}) and electrochemically active Pt surface area (ECSA= 65 ± 10 m^2 g^{-1}) towards ORR compared to commercial Pt/C electrocatalysts (Tanaka TEC10E30E) by using RDE technique. Thus, an effect of the N-doped support material on the initial ORR activity is not observed if the particles are well dispersed on the support material. In the second step, we performed various accelerated stress test (AST) studies to investigate the (electro)chemical degradation of N-doped Pt/C in 0.1 M $HClO_4$. We observed that the N-doped Pt/C shows comparable stability behaviour to the commercial Pt/C catalyst in relation to the changes in ECSA and particle growth. However, the XPS analysis signifies that the $N_{pyridinic}$ degrades much stronger than the other N surface species as a function of potential range and cycle number. For instance, after 4,000 cycles between 0.5 — 1.5 V vs. RHE the $N_{pyridinic}$ content decreases by up to 60% (from 44% to 27% of the N_{total}) and simultaneously an increase of the $N_{pyrrolic}$ content of 15% (from 44% to 53% of N_{total}) and of the $N_{graphitic}$ by up to 100% (from 10% to 20% of N_{total}) is observed. Obviously, the dynamic (cyclic voltammetry) AST protocols accelerate the degradation of $N_{pyridinic}$ compared to OCP experiments over 24 hours in 0.1 M $HClO_4$. After 24 h OCP, the $N_{pyridinic}$ decreases only from 48% to 44% of N_{total}, while $N_{pyrrolic}$ content increases by the same amount.
The combination of different AST protocols with XPS analysis reveals an advanced degradation model of different N surface groups ranging from pyridinic to graphitized N species for N-doped Pt/C catalysts under fuel cell conditions.

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Influence of the Axial, Peripheral and Non-peripheral Substituents on the Redox Properties of Subphthalocyanines: an Electrochemical and DFT Study

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A subphthalocyanine (SubPc) with a hydroxy group in the axial position and alkyl ligands ($C_{12}H_{25}$) on the non-peripheral positions, namely $(HO)BSubPc(C_{12}H_{25})_6(H)_6$, was synthesized in our lab. It contains an electron-rich macrocycle, with the lowest macrocycle-based oxidation potential of all reported SubPc molecules till date, namely 0.398 V *vs* Fc^+/Fc in DCM [1]. The ring oxidation process for molecule $(HO)BSubPc(C_{12}H_{25})_6(H)_6$ shows electrochemical quasi-reversibility, with $\Delta E = 0.084$ V (at 0.100 Vs^{-1}). A density functional theory study was conducted of $(HO)BSubPc(C_{12}H_{25})_6(H)_6$ and a series of related SubPc molecules (with peripheral and non-peripheral substituents = H, F or alkyl group; and with the axial substituent = Cl, alkoxy or phenoxy group), of which the ring-based oxidation and reduction potentials in DCM *vs* Fc^+/Fc were known [2–7]. This DFT study provided linear relationships between the first oxidation potential and HOMO energies (E_{ox} *vs* E_{HOMO}), as well as between the first reduction potential and LUMO energies (E_{red} *vs* E_{LUMO}), which can be used in future to determine the first oxidation and first reduction potential from HOMO and LUMO energies of further related SubPc molecules (and *vice versa*).

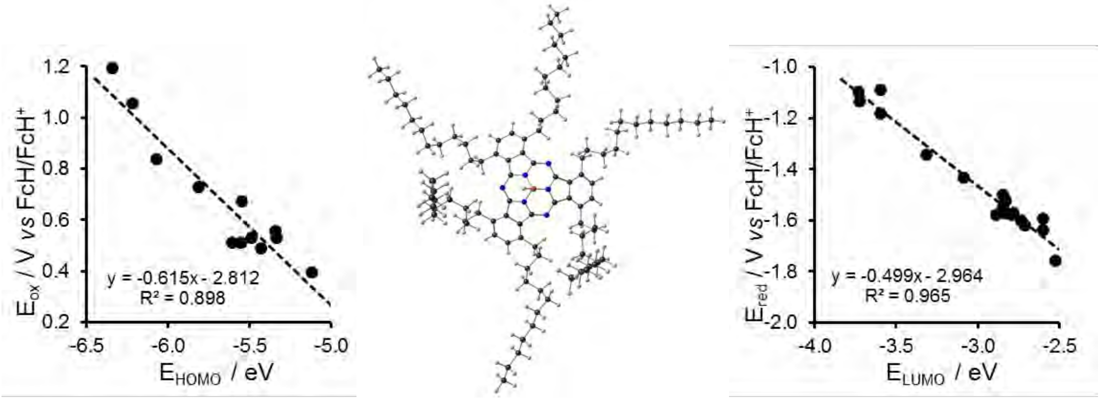

Figure: Optimized $(HO)BSubPc(C_{12}H_{25})_6(H)_6$ and relationship between the DFT energies and redox potentials.

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In situ Raman Studies of Zinc Ion Intercalation/Deintercalation Mechanism in a Rechargeable Zinc-Polypyrrole Battery in Aqueous and Bio-Ionic Liquid Electrolytes

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Because of its low cost and high safety zinc-ion batteries (ZIBs) are regarded as promising alternative to lithium-ion batteries (LIBs). [1] Inorganic materials such as MnO_2, Prussian blue analogues (PBAs) have been intensively studied as cathode materials for ZIBs. [2-4] However, these inorganic materials dissolve during the charge/discharge process, which causes loss in specific capacity during cycling. Therefore, organic materials such as polypyrrole (PPy), polyaniline (PANI) are considered as potential candidates as cathode materials. [5]

Here we present in situ Raman studies of different zinc intercalation/deintercalation mechanism in rechargeable Zn/PPy battery in aqueous and bio-ionic liquid-water mixture electrolytes. Zn/PPy battery in the bio-ionic liquid-water mixture electrolyte showed a higher specific capacity than in the aqueous electrolyte. However, a significant capacity loss was observed during cycling which was related to polymer phase transformation and zinc ion trapped into the polymer matrix. Nevertheless, the existence of bio-ionic liquid in the electrolyte helps to reduce the stain in the polymer matrix during the cycling and improve the capacity. [6]

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Novel compounds with the potential membranolytic activity.

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The discovery of antibiotics became a turning point in the struggle against infectious diseases and contributed to a significant improvement in the quality and length of human life. However, the widespread abuse of antibiotics caused that numerous bacteria have developed a resistance to their action [1]. Therefore, it is necessary to look for new, natural or synthetic active substances with a broad spectrum of antimicrobial activity and at the same time with low cytotoxicity on the eukaryotic cells. Lipopeptides appear to be one of the promising alternatives to the current antibiotics due to a completely different mode of action on bacteria cells [2]. Most antibiotics block the physiological processes of bacteria, such as the synthesis of the cell wall or DNA multiplication. In contrast, lipopeptides interact directly with the bacterial cell membrane, causing its destruction and, as a consequence, lead to cell death [3].

The interactions of two, novel synthetic lipopeptides with model lipid films mimicking bacterial cell membranes were examined. We verified whether branching in the fatty acid chain influences the mode of lipopeptide action on model bacterial cell membranes. For these purposes, three techniques were employed: Electrochemical Quartz Crystal Microbalance with Dissipation monitoring, Langmuir monolayer technique and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy. Two model bacterial membranes were used reflecting the lipid composition of gram-negative bacteria: *Escherichia coli* and *Pseudomonas aeruginosa*. For *E. coli* lipid membrane the mixture of POPE, DPPG and POPG was used, whereas *P. aeruginosa* model membrane was prepared using POPE, DPPG, POPG and cardiolipin.

EQCM-D measurements showed that both lipopeptides influence the model lipid membranes. Lipopeptides incorporate into the membranes and lead to the disordering of the lipid bilayer. Moreover, the extent of the interaction of lipopeptides depends on the branching in the fatty acid chain. Langmuir monolayer and ATR-FTIR studies confirmed that lipopeptides influence the fluidity of the lipid membranes, but the extent of this action depends on both lipid membrane composition and branching in the fatty acid chain. The combination of these techniques enabled the detailed characterization of lipopeptide-membrane interactions and *in situ* monitoring of structural changes occurring within biomimetic assembly upon exposure to the active agent.

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Electrochemical characterisation of α-hemolysin reconstituted into DMPC/CHAPSO bicelles

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Bicelles belong to the class of model membranes, which were originally developed for NMR studies. The morphology of these structures resembles the intermediate form between liposomes and micelles[1]. Additionally, the process of incorporation of protein into the bicelles is relatively simple. Therefore, we have attempted to reconstitute α-hemolysin in DMPC:CHAPSO bicelles and investigate the effect of protein on a model eukaryotic cell membrane. α-hemolysin is a toxic transmembrane protein, which creates ion channels in the membrane. In nature, the monomers of α-hemolysin bind to the cell membrane and pore assembly occurs upon collision during lateral diffusion in the bilayer[2]. Consequently, the presence of the pores leads to leakage of cellular fluid and cell death.

The process of incorporation of α-hemolysin requires a lot of space between the membrane and solid substrate. Therefore, for electrochemical measurements, we used stBLM (sparsely tethered bilayer lipid membranes) system. In the first step, we incorporated the α-hemolysin into the bicelles. Then bicelles were adsorbed on gold substrate modified with tethering molecules diluted by backfiller (1-thio-β-D-glucose). Every step was characterized by surface-enhanced infrared absorption spectroscopy (SEIRAS). Further electrochemical experiments enabled monitoring the effect of α-hemolysin on membrane hydration. The results obtained by alternating current voltammetry and electrochemical impedance spectroscopy confirmed that the presence of ion channels significantly facilitates water diffusion through the membrane. Moreover, protein incorporated in the membrane changes the potential of zero charge (pzc). The shift of pzc is around 200mV to more negative values, which may be directly related to the cell lysis.

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Realizing Highly Stable Sodium Metal Batteries with Tactically Designed Graphene Structures

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Sodium (Na) metal is a promising anode for grid-scale energy storage systems owing to its high theoretical capacity, low cost, and high earth abundance. However, the implementation of Na metal anode has been primarily hindered by Na dendrite growth and severe volume expansion that leads to low Coulombic efficiency, short lifespan and even safety issues. Therefore, it is critical to engineer the electrode-electrolyte interface and direct uniform Na deposition. Graphene, a representative of two-dimensional materials, has many unique features including chemical inertness, strong mechanical strength and tunable surface chemistry, which make it an ideal interfacial candidate to regulate Na deposition and thus suppress dendritic Na growth. By adjusting the kinetic parameters for chemical vapor deposition (CVD), graphene films can be readily tuned from single layer to multilayers, which can directly serve as coating layers to stabilize Na metal anodes. Our findings reveal that the rate capability of Na anode is critically dependent on the thickness of graphene films. Through rational design of precursor, a series of graphene films with different heteroatom dopants are synthesized to serve as substrates for Na plating and stripping. By probing the Na nucleation and growth behaviors, we revealed a binding-energy-dominated Na nucleation-growth pattern, and discovered that the strong binding affinity can decrease Na nucleation barriers and enables dendrite-free Na metal anodes. Furthermore, three-dimensional N-doped graphene microcubes can be achieved by employing sodium chloride salt as growth template. The as-grown N-doped microcubes can be directly blended into bulk Na metal to serve as solid additives, which can offer well-distributed nucleation sites to promote uniform Na deposition and minimize volume change over repeated cycles. As a result, highly stable Na metal anodes can be realized with ultrahigh capacity and rate capability over long-term cycles in carbonate electrolyte. Our works provides effective solutions to stabilize Na metal anodes from the perspective of designing CVD-grown graphene structures, paving the way towards the realization of high-energy Na battery systems.

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Three-Dimensional Porous Polyaniline Nanofibers Coated on Activated Carbon Fiber Electrodes for High-Performance Supercapacitors

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Polyaniline (PANI), a member of the class of intrinsically conductive polymers, possesses a great potential for energy storage applications, due to its tunable pseudocapacitive performance. [1,2] Yet, the understanding of its structure-property relationship is far from complete while the potential practical applications are also not fully exploited. [3]

In our efforts to close this gap, we developed a cost effective, advanced and optimized chemical oxidative route for the synthesis of three dimensional PANI nanofibers with large surface area and pore volume.

Electrodes for supercapacitors were manufactured by depositing the PANI on high surface area carbon fiber electrodes and were assembled to symmetric supercapacitors in two- and three electrode setups and in-depth electrochemical analysis including cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy was performed.

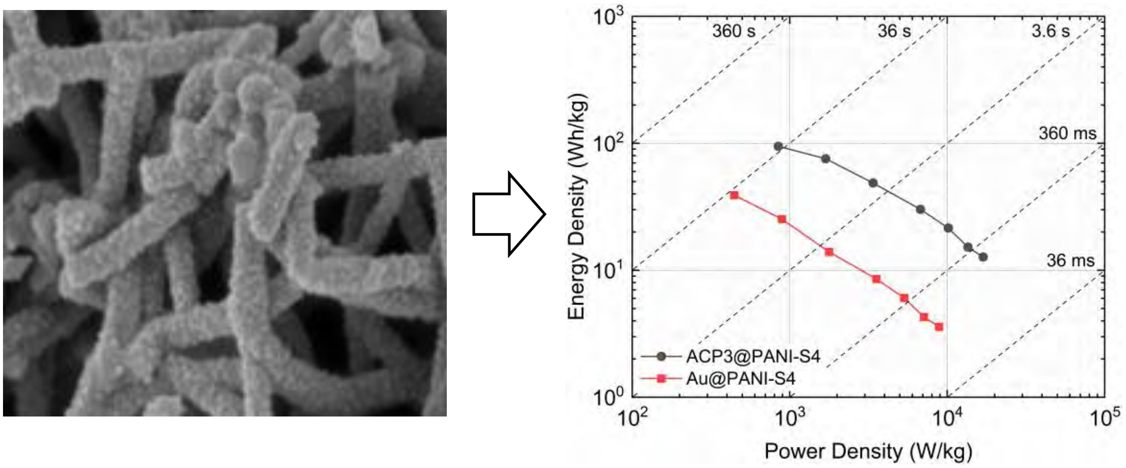

Figure: SEM image of PANI nanofibers (left); corresponding Ragone plot (right).

The overall results showed, that the various supercapacitors exhibited very good performance, rate capability and cycle stability. It is particularly interesting that the combination of the PANI nanofibers and the carbon fiber electrodes with its microporous graphene surface morphology showed a synergetic effect which resulted in a superior specific capacitance (up to 1107 F/g at 0.5 A/g), high capacitance retention (70-96%) and excellent coulombic efficiencies (92-98%).

With respect to practical applications, we believe that the presented study provides an efficient and promising way to produce electrode material with low cost, easy processability and excellent energy-storage performance.

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Visible Laser Scribing Fabrication of Porous Graphitic Carbon Electrodes: Electrochemical Properties and Applications as a Disposable Sensor Platform

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Porous graphitic carbon electrodes were fabricated by laser scribing of commercial polyimide sheets. The process was performed by a simple one-step procedure using visible wavelength laser irradiation from a low-cost hobbyist laser engraver. The obtained electrodes displayed a highly porous morphology, rich in three-dimensional interconnected networks and edge planes, suitable for electrochemical sensing applications. Spectral characterization by Raman and XPS spectroscopies revealed a crystalline graphitic carbon structure with high percentage of sp^2 carbon bonds.

Extensive electrochemical characterization performed with outer-sphere $[Ru(NH_3)_6]^{3+}$ and inner-sphere $[Fe(CN)_6]^{4-}$, $Fe^{2+/3+}$ and dopamine (DA) redox mediators showed quasi-reversible electron transfer at the graphitic carbon surface dominated by mass diffusion process. Fast heterogeneous electron-transfer rates, higher than similar carbon-based materials and comparable to other graphitic carbon electrodes obtained by infrared laser irradiation, were obtained for these electrodes.

Thin-layer transport mechanisms occurring in parallel to the main linear diffusion-limited mechanism were taken in consideration. Overall the observed enhanced electron-transfer rates effects were ascribed to the large specific surface area of the extended 3D porous network which rich in edge-planes and electrocatalytic sites. The as-fabricated electrodes were capable of differentiating the three biomarkers ascorbic acid, dopamine and uric acid in solution and selective detection of dopamine. Moreover, the compatibility with light-weight, portable and handheld instrumentation makes such electrodes highly promising for the realization of low-cost disposable sensing platforms for point-of-care applications.

Electrophoretically Deposited Bioceramic Composite Coatings on Ti Substrate Intended for Medical Use

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Bone implant materials are increasingly attracting attention in the biomaterials field. Among them, hydroxyapatite (HAP) has stood out as a prospective biomaterial due to excellent osseointegration ability, owing to its similarity with natural bone. However, due to the lack of adhesive and antibacterial properties, it is usually combined with polymers and antibacterial agents. Natural polymer chitosan (CS) was proven as an effective component of HAP-based composites, improving the adhesion and serving as a drug carrier.[1] Inclusion of antibiotics into composite biomaterials has gained a lot of attention, as it is thus possible to achieve the desirable antibacterial activity. Gentamicin (Gent) was shown to be one of the most effective antibiotics in treating bone infections. In this work, bioceramic composite HAP/CS and HAP/CS/Gent coatings were successfully assembled on Ti plates by electrophoretic deposition technique (EPD).[2] Deposition was carried out at a constant voltage of 5 V and for 12 min in a single step process from three-component aqueous suspension (Figure 1). Bioactive properties of deposited coatings were investigated *in vitro*, by immersion in simulated body fluid solution (SBF). After 7-day immersion in SBF, field emission scanning electron microscopy (FE-SEM) and Fourier transform infrared spectroscopy (FTIR) were employed to investigate the coatings' bioactivity, whereas electrochemical impedance spectroscopy (EIS) and polarization measurements were carried out during 28-day immersion in SBF in order to obtain valuable information about osseopromotive coatings' nature. Biological testing included monitoring of alkaline phosphatase activity (ALP) that is associated with the coatings' ability to promote new bone growth. The high increase in ALP activity (50 %) relative to the control pointed to the strong coatings' aptitude for the osseointegration process and new bone growth. FTIR and FE-SEM analysis gave evidence of carbonate-substituted HAP, whose presence is desirable in bone implant applications. The formation of the new apatite layer was also confirmed by electrochemical measurements pointing to the high biomineralization potential of the coatings. Antibacterial activity kinetics in suspension against *Staphylococcus aureus* and *Escherichia coli* was also monitored to examine the potential coatings' application. As expected, the gentamicin addition strongly improved the antibacterial activity of HAP/CS/Gent coating, and the effect was more pronounced against *S. aureus.*

All the obtained results potentially indicated a strong osseointegration ability of the HAP/CS/Gent coating classifying it as a promising material for bone tissue engineering.

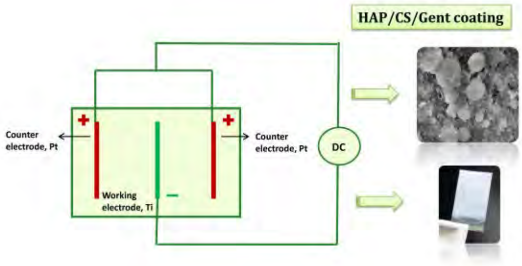

Figure 1. Electrophoretic deposition of composite HAP/CS/Gent coating

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TdT vs RCA: DNA isothermal amplifications to improve the analytical performance of aptamers

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Liquid biopsy is the most desirable but also the most challenging approach to diagnose cancer. This method relies on the presence of specific biomarkers in the accessible body fluids of cancer patients. However, many of these biomarkers are glycoproteins found in low concentration levels in a high protein content medium, the serum, thus hindering their detection. For this reason, biomarker detection requires strategies to boost sensitivity. Nucleic acid-based receptors such as aptamers are especially appropriate for this task because they can be easily manipulated with molecular biology tools such as polymerases and ligases, so they can be integrated in analytical schemes forbidden to other receptors like antibodies [1-2].

Affinity characterization is an essential step to develop reliable aptamers for tumor biomarker detection. For alpha-fetoprotein (AFP), a biomarker of hepatocellular carcinoma (HCC), two DNA aptamers were described with very different affinity. In this work, we estimate the dissociation constant of both of them by means of a direct assay on magnetic beads modified with AFP and electrochemical detection on screen-printed carbon electrodes (SPCE). Unlike previous works, both aptamers showed similar dissociation constants (Kd) values, in the subμM range. In order to improve the performance of these aptamers, we proposed the isothermal amplification of the aptamers by both terminal deoxynucleotidyl transferase (TdT) and rolling circle amplification (RCA). Both DNA amplifications improved the sensitivity and also the apparent binding constants of the aptamers. Nevertheless, this improvement depends on the true affinity of the binding pair, which ultimately limits the analytical usefulness [3].

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Graphite Felt Modified with Organic Diamines as an Anode for Efficient Microbial Fuel Cells

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Over the last couple of decades, microbial fuel cells (MFCs) have been attracting considerable attention as a promising technology that exploits microbial electrochemical activity for energy production from organic wastes and renewable biomass. This technology deals with several major issues of the modern society at once: production of sustainable energy, purification of water and/or utilization of waste.

In a MFC, electricity-generating bacteria – exoelectrogens – transfer electrons from oxidised organic compounds to an anode as the electron acceptor, and these electrons then pass through an electrical circuit and combine with a terminal electron acceptor at the cathode [1].
However, it is of crucial importance to improve the performance of MFCs before they can be scaled up, since, to date, their practical implementation is limited. The power output of MFCs is limited by the processes on the surface of electrodes, their rate and stability. Surface modification of graphite based anode materials could enhance bacterial cell adhesion, cell viability and facilitate extracellular electron transfer [2]. C-, N-, O-, and S-containing functional groups have been frequently investigated in anode surface modification for the purpose of enhancing bacterial attachment [3].

In this study, graphite felt (GF) was electrochemically oxidised and subsequent reactions with organic diamines were carried out with the aim to introduce amine group on the surface of GF. Modified GF electrodes were investigated by Fourier-Transform Infrared Spectroscopy (FT-IR) and Energy Dispersive X-Ray Analysis (EDX) techniques. Two-chamber MFCs were assembled with cathodes made of bare GF and PBS (pH 7.2) aerated with air as a catholyte. *Shewanella putriefaciens* was used as exoelectrogenic bacteria. The minimal medium was prepared as described in [4]. Sodium lactate was an electron donor. The MFCs operated at room temperature (21±1 °C).

At the end of the first 24 h period after bacterial inoculation, the MFCs reached the maximal stable values of generated voltage. Over the period of 2–7 days (25–168 h), the MFC with the anode from GF modified with *m*-xylilenediamine provided up to 45% higher voltage and current than the control MFC with bare GF, whereas the voltage and current generated by the MFC with the anode from GF modified with 2,4-diaminotoluene were 36% higher than those of the control, when electric circuits of the investigated MFCs were loaded with resistors of 659 Ω. Volume power density of the MFC with the anode from GF modified with *m*-xylilenediamine and the one with the anode from GF modified with 2,4-diaminotoluene, was approx. 2.3 and 2.0 times, respectively, higher than that of the control MFC.

It can be assumed, that bacterial adhesion of *Shewanella putrefaciens* bacteria is more favoured on the GF filaments, surface of which has been modified with *m*-xylilenediamine and 2,4-diaminotoluene.

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Electrochemical *In Situ* Method to Obtain Silver Nanoparticles in Hydrogels for Wound Dressing Applications

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The constantly evolving biomaterials fields is more and more shifting towards finding new solutions to the problem of multidrug resistant bacteria, and one of major aspects in this regard is deep and chronic wound care. Wound dressings for such a purpose have to be designed for long-term usage, and therefore must have significantly improved properties over the traditional cotton-based materials. One of the most promising directions are moisture-retentive hydrogel wound dressings, which can be tailored to meet many specific requirements of wound management and care, such as biocompatibility, debridement, gas exchange, low adherence, ease of maintenance, moisture and thermoregulation and mechanical stability.[1] Moreover, hydrogels represent ideal carrier vehicles for incorporation of antibacterial agents that are frequently loaded directly into the dressing material as this provides for quick delivery directly to the wound site and more efficient prevention of infections by skin-inhabiting bacteria, such as *Staphylococcus aureus*. Silver nanoparticles (AgNPs) are more and more used as a replacement for systemic antibiotics administration, due to the advantages such as the possibility for topical application over longer time periods without the issues of bacterial resistance. AgNPs are difficult to control and stabilize due to their high surface reactivity, but polymer-based hydrogels can be an excellent choice for their immobilization and controlled release.

In this work, we present the method to obtain physically cross linked poly(vinyl alcohol)/chitosan (PVA/CHI) hydrogels and an *in situ* electrochemical constant-voltage route to synthesize AgNPs directly inside their polymer matrix. The new electrochemical method consists of swelling the PVA/CHI hydrogel in $AgNO_3$ solution, followed by constant-voltage (90 V)-mediated reduction of Ag^+ ions in the hydrogel disc, which is placed between two platinum electrodes in a sandwich-type electrochemical cell setup (Figure 1).[2,3] The obtained AgNP-loaded hydrogels were evaluated by X-ray photoelectron spectroscopy and scanning electron microscopy in order to analyze their structure and morphology, whereas the successful incorporation of AgNPs smaller than 10 nm was confirmed using UV-visible spectroscopy, dynamic light scattering and transmission electron microscopy. Swelling and silver release behaviors were tested in phosphate buffer at 37 °C that simulated physiological conditions. Finally, *in vitro* biological validation confirmed their antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* bacterial strains, and biocompatibility towards model fibroblast cell lines (MRC-5 and L929), unquestionably indicating the strong potential of these hydrogels for wound dressing applications.

Figure 1. Scheme of the electrochemical synthesis of AgNPs inside poly(vinyl alcohol)/chitosan hydrogel

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Differential Electrochemical Mass Spectrometry studies of nitrite reduction catalyzed by Keggin polyoxometalates

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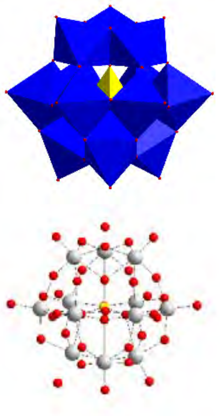
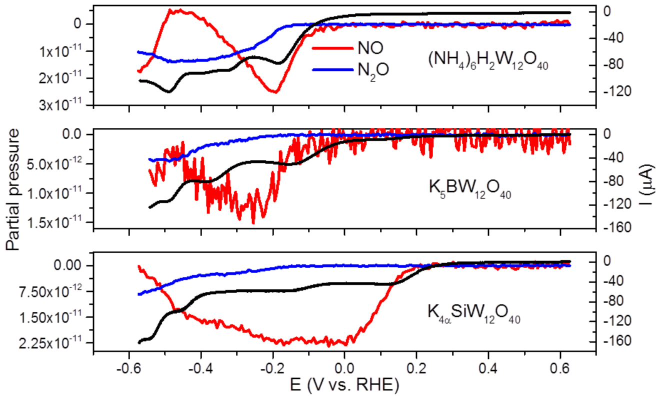
Nitrite electrochemical reduction is catalyzed, among others, by polyoxometalates (POMs), a class of inorganic metal-oxides clusters. Since early 19xx different POMs have been tested, ranging from small compounds from Keggin and Dawson families [1,2] to more complex structures (such as Wells-Dawson-derived tetramers [3], crown-type structures), and even organic-inorganic hybrids. One important issue in the electrochemical reduction of nitrite is to identify the products. Nitrite is the first product obtained from the reduction of nitrate, and both compounds are known as environmental pollutants, despite their use as food preservatives. Thus, research is conducted to convert these two species into harmless compounds. Form this point of view, disposing of an analytical technique able to rapidly identify in a single test as many products as possible becomes an important tool in the research of those catalysts that able to convert nitrite (and/or nitrate) into nitrogen. Differential electrochemical mass spectrometry (DEMS) is the analytical technique able to identify the gaseous products during one single run.

In this presentation the reduction of nitrite catalyzed by a series of polyoxometalates (POMs) belonging to the Keggin family will be discussed. The POMs were selected due to the increase in their global charge and decrease of the redox potential, from $K_4SiW_{12}O_{40}$, $K_5BW_{12}O_{40}$ and $(NH_4)_6H_2W_{12}O_{40}$ respectively. DEMS analysis was performed for these compounds for the first time in order to identify the gaseous products. An isotopically marked source of nitrite was used for the first time, i.e. the nitrogen contains 98% of isotope ^{15}N. This allowed the specific attribution to the m/z signals to products of reaction thus eliminating the possible interference from atmospheric nitrogen and carbon dioxide. Experiments were conducted at both pH 2 and 5 in order to compare the differences on the products as a function of the source compound that is either nitrous acid or nitrite. The main found gaseous products were only ^{15}NO and $^{15}N_2O$ both at pH 2 and 5. A clear relation between the formation of NO and its consumption for the production of N_2O was observed suggesting that all POMs are able to bind NO. At pH 2 the less negative potential correlated with the formation of NO is recorded for $SiW_{12}O_{40}^{4-}$ (followed by $BW_{12}O_{40}^{5-}$ and $H_2W_{12}O_{40}^{6-}$), while at pH 5, the N_2O appears at the less negative potential for $H_2W_{12}O_{40}^{6-}$ (followed by $BW_{12}O_{40}^{5-}$ and $SiW_{12}O_{40}^{4-}$).



3D view (upper) and ball-and-stick view (lower) of $SiW_{12}O_{40}^{4-}$ (Si: yellow; W: grey; O: red)



DEMS analysis of nitrite reduction catalyzed by studied POMs

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The Immobilisation and Reactivity of $Fe(CN)_6^{3-/4-}$ in an Intrinsically Microporous Polyamine (PIM-EA-TB)

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Heterogenization of homogeneous electrocatalysts is possible into polymers of intrinsic microporosity (PIMs).[1] Here, it is shown that protonation of the molecularly rigid polymer of intrinsic microporosity PIM-EA-TB can be coupled to immobilisation of $Fe(CN)_6^{3-/4-}$ (as well as immobilisation of Prussian blue) into 1-2 nm diameter channels. The resulting films provide redox active coatings on glassy carbon electrodes. Uptake, transport, and retention of $Fe(CN)_6^{3-/4-}$ in the microporous polymer are strongly pH dependent requiring protonation of the PIM-EA-TB ($pK_A \approx 4$).[2] Both $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ can be immobilised, but $Fe(CN)_6^{4-}$ appears to bind tighter to the polymer backbone presumably via bridging protons. Loss of $Fe(CN)_6^{3-/4-}$ by leaching into the aqueous solution phase becomes significant only at pH > 9 and is likely to be associated with hydroxide anions directly entering the microporous structure to combine with protons. This and the interaction of $Fe(CN)_6^{3-/4-}$ and protons within the molecularly rigid PIM-EA-TB host are suggested to be responsible for retention and relatively slow leaching processes. Electrocatalysis with immobilised $Fe(CN)_6^{3-/4-}$ is demonstrated for the oxidation of ascorbic acid.

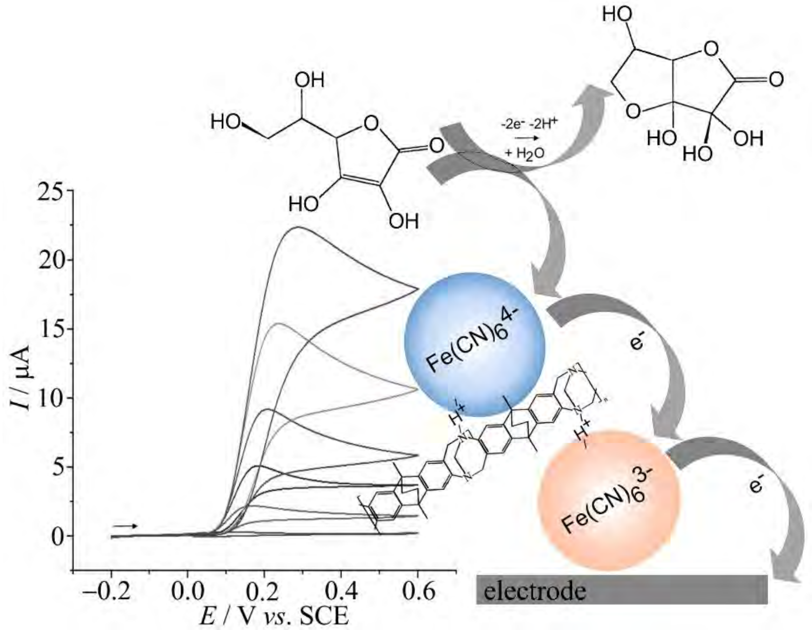

Figure 1. Schematic illustration of electron pathway of PIM-EA-TB/$Fe(CN)_6^{3-/4-}$ electrode during electron hopping and electrocatalysis application for ascorbic acid oxidation.

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Fundamental Insight into Metal Adsorption, Migration, and Electrolyte Interaction at the Alkali Metal Ion Battery Anode Surface and Interface

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Energy storage battery technologies are receiving increasing attention due to the need for a transition to a more sustainable energy economy. Alkali metal ion batteries including lithium (Li) ion batteries (LIBs), sodium (Na) ion batteries (NIBs), and potassium (K) ion batteries (KIBs), are currently being investigated, with a lot of efforts on discovering and optimizing electrode materials. Carbon materials such as hard carbons have gained considerable scientific interest as anode materials in these batteries, due to their low cost, natural abundance, and suitability for the intercalation/storage of alkali metal ions. Hard carbons are complex disordered carbon structures with randomly orientated, defective, and curved graphene nanosheets, and turbostratically stacked graphitic layers. This complex structure leads to a plethora of carbon structural motifs being present in the anode, resulting in a large number of potential morphologies. These disparate morphologies need explicit consideration when investigating the metal adsorption and migration at the anode surface, and when modelling the anode electrolyte interface. In this work we aim to shed light on these mechanisms through systematic computational modelling studies. [1–4]

Density functional theory (DFT) simulations of Li, Na, and K on different carbon motifs (defective graphene basal planes, planar graphitic layers, and curved pores) found in hard carbon anode materials were conducted to investigate their effect on the metal adsorption.[1,2,5] Our calculations show that oxygen-, and nitrogen-containing defects are energetically favorable to form on single layer carbon fragment surfaces,[5] and on curved morphologies. These defects were found to be highly beneficial for the initial metal storage, with Li, Na, and K adsorption energies greatly improved as compared to the non-defective carbon surface. Hence, it was deduced, as also suggested by experiment, that the presence of surface defects could indeed lead to a higher degree of metal storage. The effect of these defects on metal migration, which would influence the cycling properties of anode materials, was investigated through nudged elastic band calculations, and showed that metal adsorption on surface defects can lead to capacity loss and irreversible metal storage. [5]

The anode-electrolyte interface is known to have a direct impact on the battery performance. One consequence of electrolyte molecule breakdown is the presence of functional groups at the anode surface. From DFT simulations of functional groups O, OH, NH_2, and COOH at different carbon motifs (planar basal plane, H-terminated edges, and curved morphologies), we show that O-functional groups from an energetical perspective are highly probable to form on these surfaces, and can act as favorable metal storage sites. The hydroxyl group on the other hand are found to form inorganic compounds, which could contribute to irreversible capacity.

Finally, we use *ab initio* molecular dynamics (AIMD) to investigate the effect of surface roughness, disorder, defects, and termination on the electrolyte anode interactions in the ethylene carbonate (electrolyte solvent) | hard carbon (anode) system. These simulations show that solvent intercalation and breakdown is directly influenced by the anode surface termination and roughness. Furthermore, defects are found to be more probable to form in terms of defect formation energies at strained and curved carbon morphologies, and to have a direct impact on the metal binding to the anode. The effects of different structural motifs on metal adsorption, intercalation, and diffusion are investigated, to form an understanding of the anode electrolyte interfacial reactions.

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Perfluorinated Additives Improving HT-PEM Fuel Cell Performance

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Due to the dependence on fossil fuels and therefore an increase of greenhouse gas emissions and the resulting accelerated global warming, environmentally-oriented energy supplies, such as hydrogen, offer an attractive option for the deep decarbonization of our global energy systems.[1]

Fuel cells, as a local, emission-free and versatile system, have been a major research activity throughout the years. Polymer electrolyte membrane fuel cells (PEMFCs) are considered one of the most promising technologies among the various kinds of existing fuel cells. Especially high temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) can offer an improved performance due to their higher operating temperatures between 100-200 °C and therefore lead to better reaction kinetics, higher tolerance to fuel impurities and to an improved heat and power management of the system. However, some issues regarding durability and performance, such as poisoning of the platinum catalyst by phosphoric acid adsorbents, long-time stability and low oxygen solubility, are still unsolved.[2]

To overcome these difficulties we introduced planar polycyclic aromatic hydrocarbons (PAHs) to the electrode, which have a positive influence on the fuel cell system.[3] In our approach, fluorinated polycyclic aromatic hydrocarbons with specific functional groups were synthesized and integrated as additives into the electrode. Here, the specific structural features of the fluoranthene derivatives were designed to interact via π-π interactions with the porous carbon catalyst support and by their *N*-donor functionalization with the Pt-catalyst nanoparticles, to protect the active site from poisoning with phosphoric acids.
Rotating disc electrode (RDE) measurements have shown that the additives reduce poisoning of the platinum catalyst and can improve oxygen-solubility at the electrode/electrolyte interface. We have also shown that the additives can replace an additional binder, such as PTFE, for optimizing the membrane/electrode assembly. Even without PTFE, fuel cell tests have shown that the PAH additives, implemented to the electrode, increase the full cell performance significantly. The modified electrode showed double the power density compared to the untreated electrode.

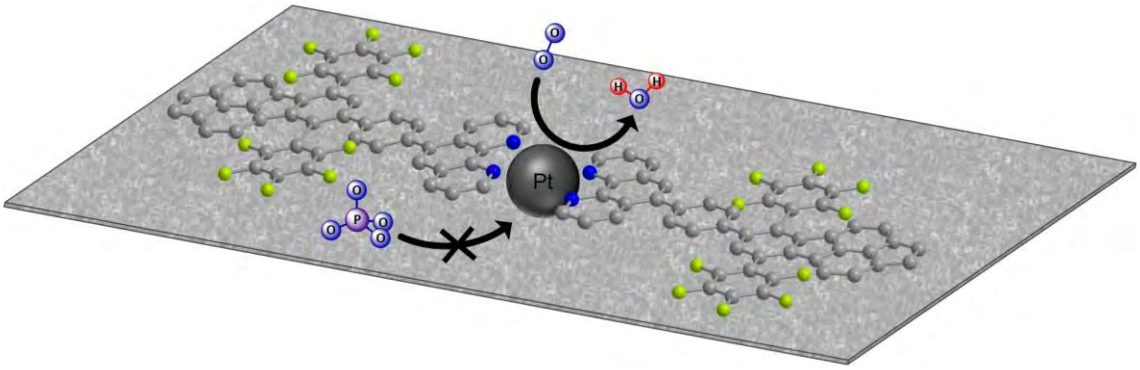

Fig. 1 Illustration of the additive-modified electrode.

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Nickel-rich Cathode Coated with Designed Binder for Cycling Performance Improvement at High-Voltage

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A cathode which is one part of a battery has a large impact on the capacity of the battery. For this reason, Ni-rich layered oxides, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) is a promising high-capacity cathode active material for high-energy density lithium-ion batteries for electric vehicles and energy storage systems. Generally, cathode is fabricated by coating the slurry of mixed active material, conductive agent and conventional polyvinylidenfluoride (PVDF) binder on aluminum current collector. NCM811 cathode coated with PVDF binder has however shown unstable cathode-electrolyte interface and structural degradation, especially, particularly under high charge voltages and elevated temperatures by fading capacity and reducing the life span of a battery. This problem originates from the physical binding mechanism of PVDF binder, which weaken the binding ability to active materials and current collector and insufficient thermal stability under harsh condition. In order to resolve those problems, we were motivated to develop a new highly functional binder as an alternative to PVDF. In this study, we present the effects of our new designed binder in improving the stability of NCM811 cathode and its performance in commercial electrolyte.

Acknowledgements

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Composition, Electrical and Optical properties of Nano Porous Titanium Oxide doped with Fe

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Anodic oxidation of Ti is a promising method to produce nano-porous oxides as photocatalysts for water splitting. Modification of the nano-porous structures via adsorption doping, pore-filling and/or deposition of material in the pores to produce effective optically absorbing and catalytic coatings is a strategic direction in contemporary photo catalysis material science.

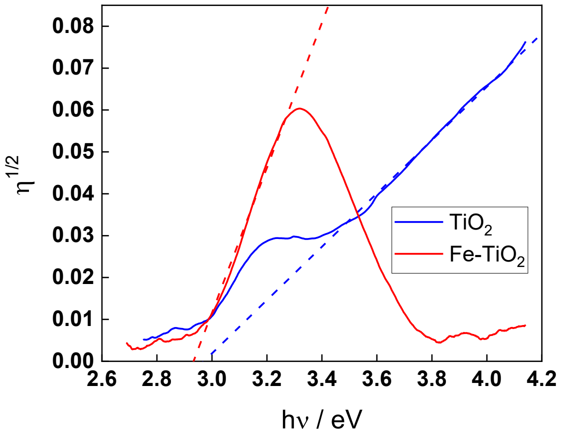

Fig. 1 Photocurrent spectra of undoped TiO_2 (blue) and Fe-doped TiO_2 (red) measured at potential of 0.3V in 0.1 M KOH

The present research reports an investigation of TiO_2 modified with Fe as prospective photocatalyst for water splitting.

Nanoporous anodic titanium oxides are synthesized in electrolytes based on ethylene glycol solvent with water and ammonium fluoride additions by anodic oxidation in a galvanostatic/tensiostatic regime (Agilent N5752A) using 99.6% Ti (Goodfellow) as working electrode and Pt mesh as counter electrode. The porosity of the oxides is estimated by re-anodization in a suitable non-dissolving electrolyte, their optical properties are assessed using diffuse reflectance spectroscopy.

Modification of the titanium oxides is achieved via anodization in electrolytes containing $K_3Fe(CN)_6$. Surface composition of oxides is studied by X-ray photoelectron spectroscopy. The conduction mechanism in such doped titanium oxides is assessed by electrochemical impedance spectroscopy. Photocurrent measurements indicate improved absorption of visible light in comparison with pristine nano-porous TiO_2 which points to prospective photocatalytic abilities of the modified oxides as photoanodes. Further optimization of the experimental conditions is needed to achieve better photo-catalytical performance.

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Molecular Understanding of Ionic-liquid-based Supercapacitors

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Electrical double layer capacitors (EDLCs), also called supercapacitors, store electrical energy via ion electrosorption directly at the electrolyte-electrode interface during the charging process, suggesting that the liquid-solid interfaces and the charging kinetics play a dominant role in the underlying energy storage mechanism and the resulting device performance. Among electrolytes used in supercapacitors, room-temperature ionic liquids (RTILs) have emerged as promising electrolytes, because of their exceptionally wide electrochemical window, excellent thermal stability, nonvolatility, and relatively inert nature. Despite considerable work on RTIL-based supercapacitors, the details of what would happen at RTIL-electrode interfaces still require in-depth exploration.

Adopting molecular dynamics simulation, we studied RTIL electrolytes with different electrodes, in comparison with the corresponding experimental measurements, to understand the energy storage mechanism underlying supercapacitors and thus to promote the design of supercapacitors. The contents of this talk would include:

1) Understanding the structural and dynamic nature of bulk RTILs at a molecular level, which would reveal the nano-aggregate, dynamics and ionic mobility, as well as the ion size impact on liquids without confinement.[1]
2) Investigating RTILs-based EDLs at open surfaces (e.g., planar, cylindrical, spherical, with defects, etc.), by integration of molecular modeling and the nano-/microscale experimental techniques (e.g., atomic force microscopy, in situ X-ray reflectivity, and neutron scattering), which would focus on the EDL structure and capacitance as well as the influence from ion size, ion type, applied potential, electrode curvature, etc.[2-4]
3) Exploring the influence of water impurity on RTIL EDLs, which would show for the first work on the adsorption of water on electrode surfaces in contact with humid RTILs and the possible strategy to reduce the water electrosorption at polarized electrodes.[5, 6]
4) Studying the capacitance and charging dynamics of RTILs in porous electrodes, which would show how conductive MOF as electrode could achieve promising capacitive performance[7] and how to tune pore size to obtain higher power density[8].

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PHOTOELECTROCHEMICAL SYSTEM WITH p- $CuBi_2O_4$

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$CuBi_2O_4$ is a p-semiconductor and has many promising physico-chemical properties including magnetic susceptibility, dielectric constant, high-temperature heat capacity, electrochemical capacitance, photoelectrochemical ability and catalytic properties In this work the spin coating method was used, which is carried out under standard laboratory conditions from aqueous salt solutions, uses the advantages of centrifugation to uniformly distribute the coating on the surface, is characterized by low material consumption, allows the formation of thin nanocrystalline layers with a given thickness. The polyethylene glycol (PEG) was used to the uniform distribution of solution droplets over the entire surface of the deposited films. A solution for depositing $CuBi_2O_4$ films was prepared by mixing copper nitrate trihydrate and bismuth nitrate pentahydrate (at 0.05M and 0.1M, respectively) with acidification with concentrated (65%) nitric acid. Subsequently, the resulting mixture was evaporated without boiling to an amount of 1/5 of the original volume and cooled to room temperature. The preparation of solutions containing polyethylene glycol - 2000 (PEG) additives was performed after cooling the initial solution, adding PEG in the amount of 0.25 grams to each 5 ml of the solution. After that, the solution was subjected to treatment in an ultrasonic bath. The centrifugation procedure with rotation during 90 s. at a frequency of 500 rpm.on support glass/FTO wascarried out. After application, the films were annealed in a muffle furnace for 2 hours at a temperature of 600°C. Photoelectrochemical studies were performed in real time in a solution of 0.2 M Na_2SO_4 + 0.1 M phosphate buffer + 10 mM H_2O_2 under modulated illumination with a wavelength of 465 nm in a GillAC (ACM Instruments) apparatus using a quartz cuvette and a silver chloride reference electrode.

Surface micrographs showing the ordering of the growth of $CuBi_2O_4$ particles (size ≈200 nm) with the addition of polyethylene glycol to the solution were obtained by SEM. The results of AFM indicate 1.5 times decrease in the roughness of the relief and the formation of equidimensional rounded crystallites. For all films, the XRD method confirmed the presence of the crystalline Kusachiite phase corresponding to the $CuBi_2O_4$ compound. Comparative analysis of the XRD diagram of samples obtained from solutions containing PEG and "pure" (without PEG) shows an increase in the number of peaks and their intensity in the first case. Based on photoelectric measurements, it is established that $CuBi_2O_4$ films precipitated from solutions containing polyethylene glycol show a photoactivity of 2 times higher. Thus, the developed method of deposition of a complex copper-bismuth $CuBi_2O_4$ system makes it possible to obtain polycrystalline films with high photosensitivity, p-type conductivity, which are promising for use in photoelectrochemical converters as photocathodes.

Electrochemical Synthesis of (Hydro)oxides for Oxygen Evolution

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Electrochemical water splitting is a promising technology for hydrogen production and sustainable energy conversion, but the currently available electrolyzers still require highly active and robust anodic electrodes for the oxygen evolution reaction (OER). In this talk, we focus on two electrochemical synthesis strategies for (hydro)oxide design and water oxidation applications. On the one hand, we developed a universal electrodeposition method for synthesizing of metal hydroxides/oxides on varied substrates via reduction of oxyacid anions. On graphitic substrates, we find that the insertion of nitrate ion in graphene layers significantly enhances the electrodeposit–support interface, resulting in high mass loading and low interface resistance. For the electrocatalytic OER, the nanocrystalline cerium dioxide and amorphous nickel hydroxide co-electrodeposited on graphite sustains long-term robust durability (over 300 h) at a large current density of 1000 mA cm^{-2}. On the other hand, an electrochemical reduction etching method has been developed for controllable tailoring of the cationic defects in iron-based oxides under mild conditions. The optimized defective spinel-type iron nickel oxide exhibits an overpotential as low as 270 mV at 10 mA cm^{-2} and a Tafel slope of only 33.8 mV dec^{-1} for the OER, outperforming the benchmark RuO_2 and pristine oxide. Experimental investigations and theoretical calculations further demonstrate that the presence of iron defects increases the Ni–O covalency that promotes the adsorption and activation of H_2O, modulates surface electronic structure that endow moderate oxygen intermediate species adsorption, promote electron transfer, and enrich active sites, thus boosting the OER activity. These results provide new and effective electrochemical methods for synthesis and construction of efficient OER eletrocatalysts.

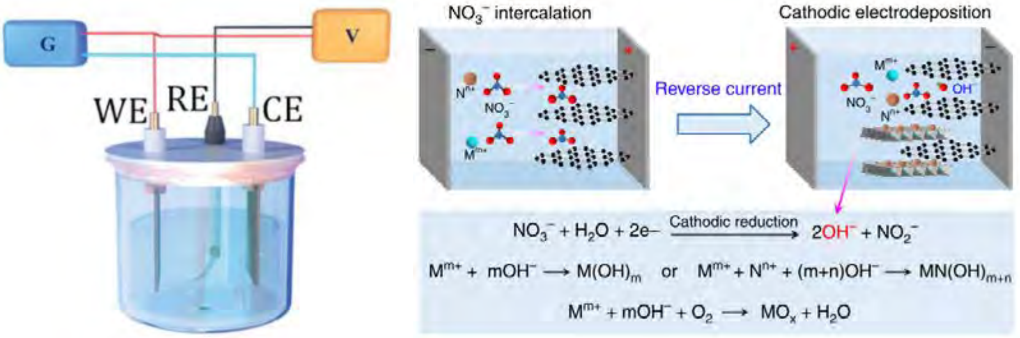

Fig.1 Electrodeposition strategy and principles.

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Tailoring Heterojunction Architecture on IrO_2 Based Dimensionally Stable Anodes for Environmental Applications

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Dimensionally stable anodes (DSAs), most often based on IrO_2 as a core component, have been widely utilized for industrial chlorine production (chlor-alkali) and high-salinity wastewater treatment via generation of reactive chlorine species (RCS). For an effective electrochemical water treatment, a competition between oxygen and chlorine evolution reactions for the surface coordinated reactive oxygen species would be an important consideration. This study reports variable strategies on heterojunction architecture over the conventional DSA configuration to enhance reactive chlorine species (RCS) generation in dilute aqueous solution in terms of current and energy efficiency. Firstly, we investigated the effects of TiO_2 over-layers with variable loadings on $Ir_{0.7}Ta_{0.3}O_x$ anodes. The $IrTaO_x$ layer was found to serve as ohmic contact with the Ti substrate by redox cycle of Ir(IV)/Ir(VI) couple, while the outer TiO_2 layer could shift the heterogeneous reaction selectivity. In particular, an elevated concentration of adsorbed hydroxyl radical could enhance the rate of RCS generation. Secondly, we demonstrated that bismuth titanate outer layer on the $IrTaO_x$ layer could significantly enhance the current and energy efficiency of reactive chlorine generation, while allowing •OH mediated oxidation in the absence of the chloride ion. In particular, formation of $Bi_2Ti_4O_{11}$ was noted at Ti:Bi ratios of 5:5 and 3:7 in precursor. Considering relatively low electrical conductivity of TiO_2 and Bi_2O_3 as well as the instability of Bi_2O_3 in circum-neutral pH, our findings would boost the efficacy of IrO_2 based DSA with minimal losses in current generation and operation lifetime.

Keywords: Heterojunction electrode, electrochemical chlorine generation, water treatment

Pd- and Pt-Polypyrrole coated Nitrogen-doped Reduced Graphene Oxide for Voltammetric Sensing of Formaldehyde

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The study presents the synthesis of polypyrrole-coated palladium platinum/nitrogen-doped reduced graphene oxide nanocomposites (PdPt-PPy/N-rGO NC) via direct the reduction of Pd(II) and Pt(II) in the presence of pyrrole monomer, N-rGO and L-cysteine as the reducing agent. X-ray diffraction confirmed the presence of metallic Pd and Pt from the reduction of Pd and Pt cations. Transmission electron microscopy images revealed the presence of Pd, Pt and PPy deposition on N-rGO. Impedance spectroscopy results gave a decreased charge transfer resistance due to the presence of N-rGO. The nanocomposites were synthesized with different Pd/Pt ratios (2:1, 1:1 and 1:2). A glassy carbon electrode (GCE) modified with the nanocomposite showed enhanced electrochemical sensing capability for formaldehyde in 0.1 M sulfuric acid solution. Cyclic voltammetry showed an increase in the formaldehyde oxidation peak current at the GCE modified with Pd2Pt1 PPy N-rGO. At a typical potential of 0.45 V (vs. SCE), the sensitivity in the linear segment was 345.8 μA.mM $^{-1}$. cm^{-2}. The voltammetric response was linear between 0.01 and 0.9 mM formaldehyde concentration range, with a 27 μM detection limit (at S/N = 3).

Keywords: Voltammetric sensing; Polypyrrole; Nanostructure; Nitrogen-doped reduced graphene oxide; Formaldehyde sensor

Towards Personalization of Electropolishing Post-Treatments

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The present study investigates the possibility of introducing the concept of mass personalization to electropolishing treatments. The goal of product personalization is to cater to the unique preferences of the customers by close integration of them in the design process (1-2).

Electropolishing is among the flexible industries that are suited to the concept of personalization because it presents a relatively small machining overhead. It enhances the aesthetics and durability of metal parts by smoothening and brightening of their surface (3-4). The flexible yet effective nature of electropolishing makes it highly appealing to many applications, especially industries such as watchmaking that can benefit from the aesthetically pleasing metal surfaces as well as the possibility of demanding different surface appearances. Such industries need to adopt strategies to increase their level of product customization to maintain their competitiveness in today's market. Electropolishing services offered nowadays do not offer diverse options at least in terms of the appearance of the final surface, much less the possibility of providing the customer's specific selection of surface gloss. There seems to be a huge potential in customization of the electropolishing services, where the process can be tuned in order to achieve the specific surface finish demanded by the customer.

In this study, various surface finishes are obtained for stainless steel 316L and grade 5 Titanium samples, which are two of the most used alloys by the watchmaking industry. In order to achieve different surface roughness and brightness, some electropolishing parameters (time and electric potential) are modified.

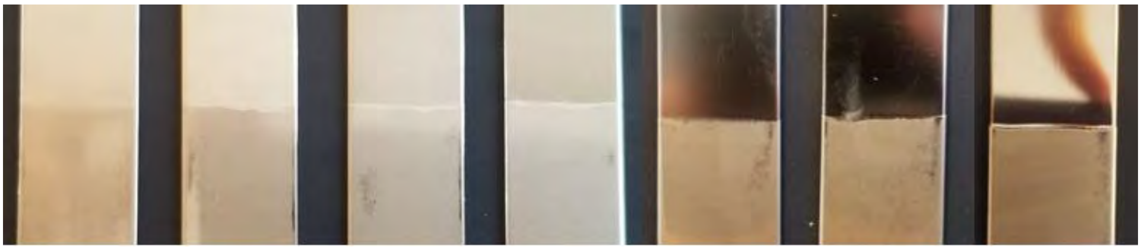

Figure 1. Various surface finishes achievable for Stainless Steel 316 L samples, by electropolishing at different times and applied potentials

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Moderate Oxophilic CoFe in Carbon Nanofiber for the Oxygen Evolution Reaction in Anion Exchange Membrane Water Electrolysis

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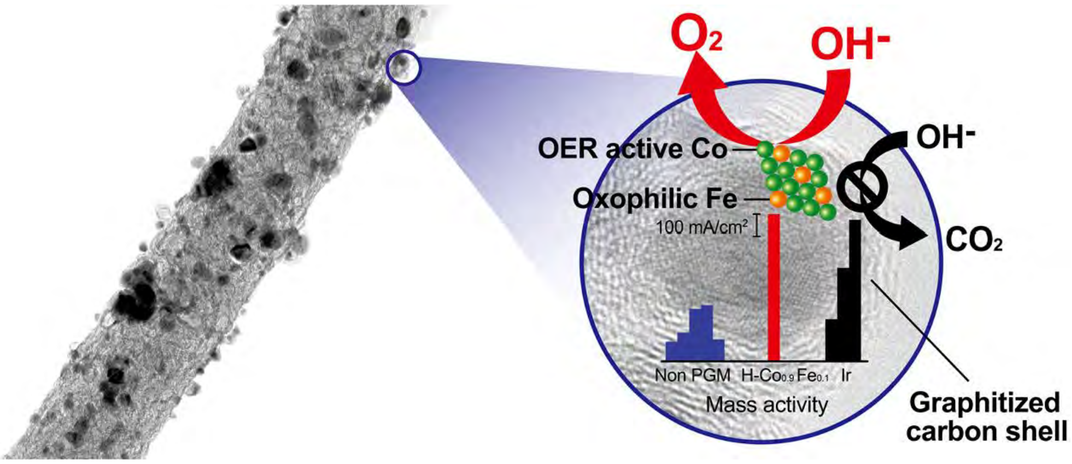
We propose corrosion-resistant carbon-coated $Co_{0.9}Fe_{0.1}$ alloy nanoparticles as highly active and durable electrocatalysts for the oxygen evolution reaction (OER) in anion exchange membrane water electrolysis (AEMWE). In the presence of 10% Fe atoms, the oxophilicity of Co metal is modulated in a direction to facilitate OH^- adsorption on Co^{3+}; thus, $Co_{0.9}Fe_{0.1}$-carbon nanofiber (CNF) can exhibit smaller overpotentials than other metal ratios in $Co_{1-x}Fe_x$-CNF. Additionally, we confirm catalytic degradation from the oxidation of the carbon layer, which is triggered by defects in the carbon originating from Fe during the pyrolysis step. The $Co_{0.9}Fe_{0.1}$ metal is further optimized by increasing graphitization to simultaneously achieve superior activity and durability for application on AEMWE. This work not only demonstrates the role of Fe in Co metal for controlling the proper oxophilicity but also shows the importance of graphitized carbon as a catalyst support for stable water oxidation.



The Influence of O_2 and Local Changes of pH on Pt Oxide Formation

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The effect of oxide coverage on the oxygen reduction reaction has been widely studied and it has been reported that a partially oxidised surface is less electroactive towards the ORR than a fully reduced metallic surface. In contrast, the effect of molecular oxygen on oxide formation and reduction has not received much attention, probably due to the difficulty to separate the contribution from both processes that occur at similar potentials and time scales. Some groups have studied this by forming oxide in the presence of molecular oxygen and reducing it in its absence; this requires precise control to change the solution or to fully degas it before the reduction takes place. Furthermore, these experiments do not take into account the different states of the surface due to the availability of molecular oxygen. Recently, our group reported the presence of oxygenated species that are pre-adsorbed on metallic electrodes after being exposed to oxygen (1, 2). Recent results in neutral media suggest that these species are related to oxide formation that could be influenced by the presence of molecular oxygen in solution and by local changes of pH. To study this, we exploit the negative feedback mode of SECM and control the tip/substrate distance to minimise the influence of dissolved oxygen on the reduction response; this procedure also ensures that the state of the surface is the same since it is always exposed to oxygen. The results in acidic conditions show a good correlation between the oxide coverages obtained under hindered diffusion and the coverage obtained in a fully degassed solution, suggesting that the oxide formation is not influenced by the presence of dissolved oxygen at low pH. In neutral and unbuffered media the oxide formation shows a dependence on the tip/substrate distance. Furthermore, under hindered diffusion we observe a diffusion controlled wave that we ascribe to OH^- oxidation; this suggests that the differences seen in the oxide formation region in the presence and absence of oxygen are due to local changes of pH. Overall, we show that Pt electrochemistry is not influenced by the presence of O_2 in solution as previously reported, but by the local changes of pH that occur during reactions under neutral and unbuffered media.

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Consecutive Ag^{I} Ion Incorporation into Oligonucleotides containing Cytosine-Cytosine Mispairs

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Metal ions interact with DNA at various sites and play an essential role in stabilizing the diverse possible confirmations. In particular, Ag^{I} binds to bridges the nucleobases, effectively putting it within the double helix, instead of phosphate backbone, and it is selectively captured by cytosine-cytosine mispairs in the DNA duplex. Herein, we have demonstrated the consecutive incorporation of Ag^{I} ion into the dsDNA containing adjacent C-C mispairs and the corresponding conformational effects on the overall duplex conformation. Our ultraviolet (UV) and circular dichroism (CD) spectroscopy studies have shown that a stable bridging of C-Ag^{I}-C upon the incorporation of the stoichiometric amount and significant structural changes in the presence of an excess amount of Ag^{I}. Subsequently, the Ag^{I}-mediated DNA strands are immobilized on Au surfaces, and their electrochemical properties are monitored using CV, EIS and SECM showing increased overpotentials and charge-transfer resistances and decreased the rate constant in the presence of an excess of Ag^{I}, respectively, which are linked to dramatic structural changes. These results are further supported by the XPS and sulfide-Au reductive desorption measurements. Our findings demonstrate that metal ion mediation of nucleobase mispairs plays an important role in the conformational stabilization of DNA duplexes and to change their electrochemical properties, two facts indispensable to the study of DNA and DNA based sensors.

Combustion synthesis of La-perovskites for fuel cell reactions

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High energy density technologies of fuel cell and metal air batteries are considered as the energy conversion and storage systems to meet the future energy requirements. These technologies are greatly dependent on a pair of sluggish electrochemical reactions such as oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Both reactions require high cost metals to enhance the activity and stability, but their availability and cost limits the worldwide application in electrochemical technologies. Recently, a new class of materials, perovskites, have shown great potential for energy conversion and other relevant applications. In this paper, I plan to discuss the synthesis and electrocatalytic property evaluation of lanthanum based perovskites. Combustion based techniques were used to synthesize $LaMO_3$ (M=Cr, Mn, Fe, Co, Ni) perovskites by using metal nitrate precursors in presence of glycine fuel [1]. The structural and morphological properties of the catalysts were studied using XRD, SEM, and TEM. The synthesis conditions are found to have a significant effect on the nature of the nanoparticles and it can be tuned to synthesize amorphous or crystalline materials. The perovskites showed exceptional performance for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline medium. $LaMnO_3$ is found to be most active for ORR, whereas $LaCoO_3$ for OER. The onset potential of $LaMnO_3$ is -0.12 V, and for other La-transition metals is nearly -0.2 V. The Koutechy-Levich plot obtained from rotating disk electrode shows a higher number of electron transfer for $LaMnO_3$ catalyst and the least for $LaCrO_3$, whereas the stability results indicate the $LaCoO_3$ to be more stable as compared to $LaMnO_3$. Based on the experimental results and literature survey, it is suggested that the improved activity of Mn and Co based lanthanum perovskite catalyst could be due to the optimum stabilization of reaction intermediates involved in the rate-determining step (RDS) of ORR/OER.

Another aspect of this paper is based on a novel approach to the synthesis of perovskites. Addition of a small quantity of leachable salts during combustion helps in creating a thin coating of salt around the nanoparticles, in addition to lowering the combustion temperature resulting in smaller crystallites. Post combustion leaching of the salts results in agglomeration controlled smaller nanoparticles with high surface area and oxygen deficient surface cites suitable for electrocatalytic applications. Initial results indicate approximately two-fold increase in the kinetic current density of $LaMnO_3$ after salt assisted synthesis [2].

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Indirect Photo-electrochemical Detection of Carbohydrates Mediated by Hydrogen and Enhanced by a Polymer of Intrinsic Mircoporosity

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An “indirect” photo-electrochemical sensor is presented for measuring a mixture of analytes including reducing sugars (e.g. glucose, fructose) and non-reducing sugars (e.g. sucrose, trehalose). The novelty is in the employment of a palladium film creating a two-compartment cell to separate the analytical compartment and electrochemical responsive compartment (see Figure 1). The photo-catalytic compartment relies on a well-known photocatalyst Pt@g-C_3N_4[1] immobilised into a polymer of intrinsic microporosity (PIM-1)[2]. The immobilised photocatalyst is deposited onto a thin palladium membrane, which allows rapid pure hydrogen diffusion. When applying blue LED light, hydrogen is generated driven by quenchers, captured by the polymer coating, and then driven across the palladium foil. Chronopotentiometry (zero current) responses from the localized photo-driven production are observed in the electrochemical compartment. This concept demonstrated potential to measure any types of hole-quenching analytes with no conductivity or buffer requirements. Potential for applications of “indirect sensing” is demonstrated with commercial soft drinks. This design is proposed to pave the way for sensing applications studying complex samples like colloids, foods, formulations, or drugs without any directly applied electrochemical process.[3]

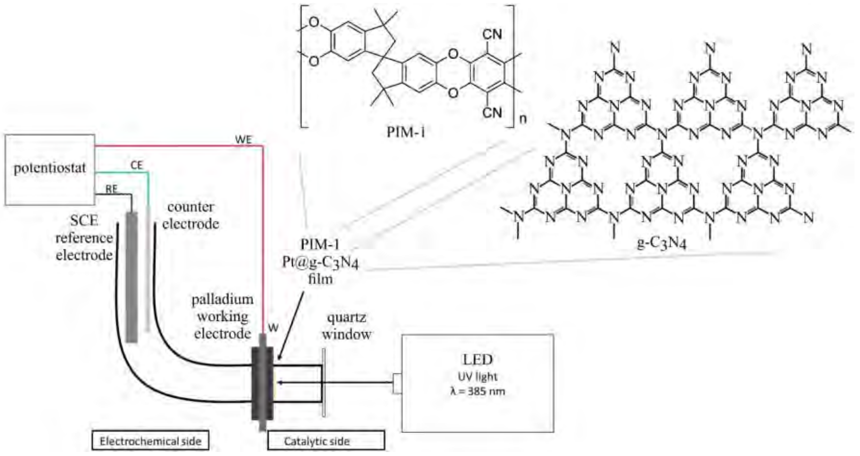

Figure 1. Schematic illustration of an experimental direct photo-electrochemical sensor.

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Enzymatic Biofuel Cells for Controlled Drug Release

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Self-powered drug delivery systems based on conductive polymers (CPs) that eliminate the need for external power sources, are of significant interest for use in clinical applications. Osmium redox polymer mediated glucose/O_2 enzymatic biofuel cells (EBFCs) were prepared with an additional CP-drug layer on the cathode. On discharging the EBFCs in the presence of glucose and dioxygen, model drug compounds incorporated in the CP layer were rapidly released with negligible amounts released when the EBFCs were held at open circuit. Controlled and *ex situ* release of three model compounds, ibuprofen (IBU), fluorescein (FLU) and 4',6-diamidino-2-phenylindole (DAPI), was achieved with this self-powered drug release system. DAPI released *in situ* in cell culture media was incorporated into retinal pigment epithelium (RPE) cells. We present a proof-of-concept responsive drug release system that may be used in implantable devices.

Industry 4.0: Model Sized Smart Factory for Electropolishing

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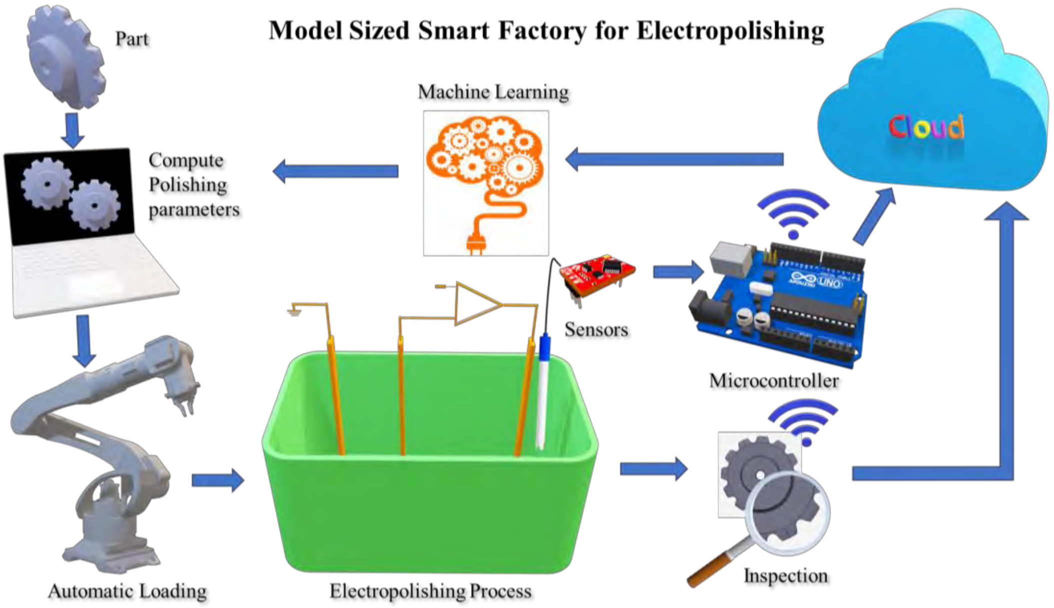
Abstract:

With the arrival of Industry 4.0, manufacturing industries are initiating the manufacturing process through the latest smart technologies, which allows them to make faster, smarter, more confident decisions. Notably, the small and medium-sized industries are moving their manufacturing facility to smart factories. However, most of the electropolishing industries do not have enough know-how and assets to build high technology like smart factories. In fact, automation and smart technologies are almost non-existent in industrial electropolishing. As a result, the industry is facing problems in terms of automation, long term quality control, and data collection. This paper proposes a model sized automated smart manufacturing setup for the electropolishing manufacturing process in the laboratory environment. The proposed model sized manufacturing setup has automated loading & unloading of workpieces, real-time monitoring of bath parameters (such as bath temperature, pH, electrical conductivity, density, and viscosity) and machine to machine communication without the need for human intervention. The process parameters information is stored and processed in a cloud. We employed a machine learning approach to adjust the process parameters of electropolishing to maintain consistent quality and repeatability of manufacturing products using the long-term history of data. Finally, the performance of the model sized smart factory is analysed from the viewpoint of real-time monitoring of bath parameters, machine to machine communication, and consistent quality of the product. The results show that the system is effective in the monitoring of bath parameters and delivers consistent quality.



3D printed electrodes for fuel electroanalysis: Simultaneous determination of lead (II) and copper (II) in ethanol

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In this work, we report a simple and sensitive protocol for the simultaneous sensing of lead and copper at low levels in liquid fuel samples (bioethanol) by square-wave anodic stripping voltammetry (SWASV) at a carbon black/polylactic acid (CB/PLA) 3D-printed working electrode. A 3D printing pen was used to fabricate the working electrode in a similar design to a conventional disc electrode. The CB/PLA electrode was treated by the application of a potential of +1.4 V per 200 s and then by -1.0 V for the same time in 0.5 mol L^{-1} NaOH. The CB/PLA surface treatment dramatically improved the electrochemical response of copper and lead as shown in Figure 1, probably exposing the CB conducting sites of the 3D printed surface. The parameters that affect the SWASV technique for the determination of metals in the hydroethanolic samples were carefully optimized using univariate and multivariate designs. Under the optimized conditions, wide linear ranges were observed up to 200 µg L^{-1} ($R^2 = 0.991$) for lead and up to 400 µg L^{-1} ($R^2 = 0.995$) for copper. The limits of detection (LOD) were estimated as 1.0 and 1.7 µg L^{-1} with sensitivities of 0.0054 and 0.0047 µA µg L^{-1} for lead and copper, respectively. The inter-day (n=3) and interelectrode (n=2) studies provided RSD results lower than 2.8%, showing good stability of the proposed CB/PLA 3D-printed sensor in hydroethanolic medium with 30% (v/v) ethanol. The proposed protocol was applied to determine lead and copper in fuel ethanol samples, which were just diluted in the supporting electrolyte (HCl). Recovery values for two fortified samples in three different levels of lead and copper ranged from 82% to 107%. The developed method is feasible to be applied for the quality control of automotive (bio)fuels in gas stations (in-loco analyses) and the use of the CB/PLA 3D-printed working electrode makes this protocol very attractive in terms of cost-effectiveness and sustainability as low volumes were used and the 3D-printed electrodes are biodegradable. Figure 1 shows

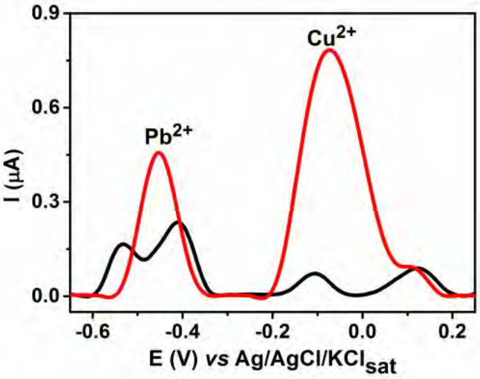

Figure 1. Baseline-corrected SWASV recordings for Pb^{2+} and Cu^{2+} (both 100 µg L^{-1}) before (black line) and after (red line) electrochemical treatment. SWASV conditions: deposition time: 180 s; deposition potential: -1.1 V; stirring rate: 1500 rpm; conditioning potential: +0.6 V; conditioning time: 30 s; step potential: 1 mV; modulation amplitude: 40 mV; frequency: 10 Hz. Supporting electrolyte: ethanol:water (30:70%; v v^{-1}) containing 0.1 mol L^{-1} HCl.

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Assessing the Reactivity of Polyphenolic Antioxidants with Electrochemically Generated Superoxide Anion Radical by Cyclic Voltammetry

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Electrochemistry is a valuable tool that has been used to study the interaction between reactive oxygen species (ROS) and antioxidant compounds, such as phenols.[1-3] ROS, such as the superoxide anion radical, $O_2^{\cdot -}$ (SAR) is naturally produced within the biological environment *via* a single electron reduction of molecular oxygen (O_2).[2,4] Excess ROS can contribute to oxidative stress leading to cellular death and to the onset of health issues, such as cancers, diabetes and neurodegenerative diseases.[1,2,4] Flavonoids, such as quercetin (QCR), are polyphenolic compounds with antioxidant properties which react with SAR, further preventing cell damage.[3-5] Biologically relevant metal ions are also known to regulate ROS activity *via* Fenton reactions.[4] Interactions between flavonoids with metal ions, and the role of metallo-flavonoid complexes on the antioxidant capacity and activity remains poorly understood.[4,5] Using a three-electrode electrochemical cell, cyclic voltammetry (CV) was carried out to identify antioxidant activities of QCR and its metal ion complexes. A glassy carbon working electrode, a Pt wire counter electrode and an $Ag/AgNO_3$ reference electrode immersed in DMF were used to generate the $O_2^{\cdot -}/O_2$ redox couple electrochemically *in-situ*.[2] The current and potential associated with the $O_2^{\cdot -}/O_2$ redox couple were monitored to measure and quantify the scavenging ability of metal ions (Fe^{3+} or Cu^{2+}), QCR and their metallo-QCR complexes. In addition, *in-situ* or preformed metallo-QCR complexes were also tested and compared. CV data indicated that all additives played a role as free radical scavengers and decreased the concentration of SAR in solution. Overall, the copper-QCR complexes induced greater reduction of SAR concentration compared to the iron-QCR complexes.

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Performance modelling and design of the electrode microstructure for batteries using a 3D pore-scale lattice Boltzmann model

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The 3D microstructure of porous electrodes plays an important role in the performance of electrochemical energy devices including fuel cells, batteries and electrolysers. Computational models are useful as they can provide a direct link between microstructure properties and the complex transport phenomenon and electrochemical performance [1]. A three-dimensional (3D) pore-scale lattice Boltzmann modelling (LBM) framework has been developed at University of Surrey to simulate the transport mechanisms of gases, liquid electrolyte flow, species and charge in the porous electrodes [2-4], coupled with electrochemical reactions.

In this paper, we will show the application of the 3D pore-scale LBM framework for modelling 3D porous fibrous electrode microstructures in redox flow batteries (RFBs), with electrochemical reactions implemented at the interfaces between the solid fibres and the liquid electrolyte. The model is able to capture the multiphase flow phenomenon and predict the local concentration for different species, over-potential and current density profiles under charge/discharge conditions [3]. It is found that the electrochemical performance is reduced with air bubbles trapped inside the electrode [3]. To validate the model, the simulated pressure-drop and electrochemical performance are compared against the experimental measurement based on the same electrode structures [4]. Three electrode structures (SGL paper, Freudenberg paper, Carbon Cloth) are reconstructed from X-ray computed tomography (CT). These electrodes are used in an organic aqueous RFB based on TEMPO. Excellent agreement is achieved between the simulated and experimentally measured electrochemical performance, indicating the validity of our model [4]. The effects of different porous structures on the performance are also investigated, to reveal the desirable electrode microstructural features for RFBs.

We will also report the application of 3D pore-scale LBM framework for simulating lithium-ion battery (LIB) electrodes [5]. The model is further developed to simulate the complex transport processes of ions, electrons, and multicomponent liquid species in real electrode geometries, and predict electrochemical performance. The simulated discharge curves of a realistic nickel-manganese-cobalt (NMC) battery electrode are in good agreement with the experimental measurement, demonstrating the validity of the model. The LBM framework is then applied to simulate a series of electrode structures generated using a discrete element method, to understand the effects of particle size and distribution, porosity, surface area, and tortuosity on the performance of the electrode. It is revealed that surface area and porosity are the determining factors for the performance, and structured patterns are beneficial for achieving uniform local distribution of lithium and current densities within the electrode. The current modelling work enhances our understanding of the impact of electrode microstructure on electrode performance, leading to design principles for electrodes with optimal microstructure for LIBs applications.

Finally, we will report our recent work on using the 3D pore-scale LBM framework to help design 3D porous carbon structures as lithium host, to suppress Li dendrite growth and enable long cycle life for lithium metal batteries (LMBs).

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Model-Based System Design of Alkaline Water Electrolyzers Powered by Renewable Energy

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Alkaline water electrolysis is a key technology to utilize increasing amounts of fluctuating and intermittent renewable energy. Conventional alkaline water electrolyzers are designed for a stationary operation at fixed process conditions. Therefore, this technology needs to be enhanced to handle the required dynamic operation. The main problem of existing systems is the limited part-load range. Below 10 – 20 % of the nominal load, the gas purities decrease significantly. As hydrogen and oxygen can form explosive mixtures in a very broad range, this is a major safety issue. In consequence, electrolyzers perform a safety shutdown when reaching a gas impurity of 2 vol.% hydrogen in oxygen, which is 50 % of the lower explosion limit [1]. An additional problem is the electrode degradation due to an increased number of on/off cycles [2]. Furthermore, the system temperature needs to be in a fixed range for an efficient operation. Since most electrolyzers powered by renewable energy do not provide a heating unit, only the heat generation of the reaction is used to maintain a suitable temperature. Hence, the system inertia defined by the liquid electrolyte volume should be optimized for the local conditions [3]. As this parameter also influences the product gas purity, an optimal sizing without an adequate process model is difficult.

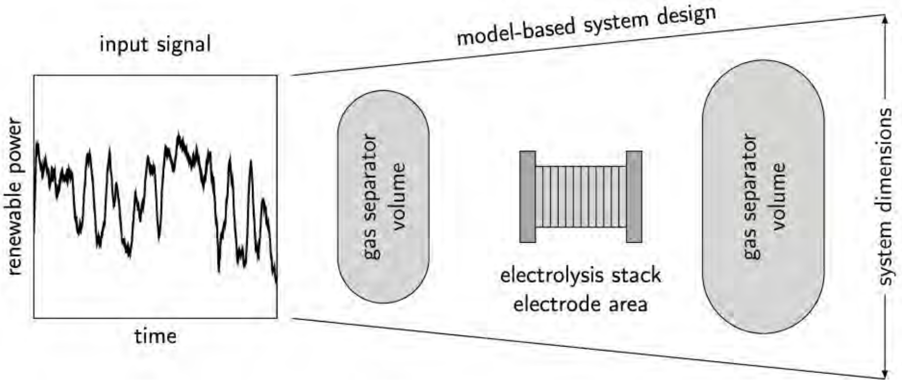

Figure 1: Scheme of model-based system design. Location depended availability of renewable power can be used to determine the optimal system dimensions.

This contribution shows how model-based system design can help to improve the overall system performance and production availability. Since every location offers different conditions, the electrolyzer must be adapted accordingly. A mathematical model is used, which extends an existing approach by implementing dynamic balance equations, pressure effects and concentration drifts [4]. Model validation is performed by stationary and dynamic experiments in a lab-scale electrolyzer. In Figure 1, a typical fluctuating wind power profile is provided, which can be utilized to optimize the system dimensions. The combination of suitable system designs and dynamic operation strategies enables longer production periods by enhancing the gas purity. As a result, more renewable energy can be used and the system components benefit from a longer lifetime. Whereas the local renewable energy production rate determines the nominal load, the fluctuation amplitude and frequency can be used to calculate the optimal system dimensions.

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Insights into the ORR and OER in Ca^{2+} containing DMSO: A DEMS, RRDE, AFM and XPS study

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Calcium, being the fifth most abundant metal on earth, combines high abundance with competitive volumetric capacity. As newer studies show promising results concerning electrochemical Ca plating/stripping (1-5), a combination with an oxygen cathode promises impressive theoretical energy densities. In literature some pioneering work on the Ca $–O_2$ system exists (6-8) but deeper fundamental research is necessary to get insights into the reaction mechanism of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).

In this study we are investigating the ORR and OER in Ca^{2+} containing system with various electrochemical and analytical methods. The product distribution of ORR products is investigated with differential electrochemical mass spectrometry (DEMS) and rotating ring disc electrode (RRDE) using Pt and Au as electrocatalysts. The main products are Ca-peroxide and Ca- superoxide. Both products are soluble in DMSO. A complete blocking of the electrode surface, as it is known from $Li-O_2$ literature, was not observed. Still the formation of superoxide in presence of the deposited film on the electrode is observed. Characterization of the ORR products was done via ex situ XPS measurements. There we could confirm calcium peroxide and calcium superoxide as ORR products. Another oxygen containing product seems to be calcium oxide, which is located close to the electrode (shown by Ar^+ etching and XPS). In the electrochemical experiments the electrocatalysts can fully be regenerated by applying higher electrode potentials as XPS studies showed. In addition the deposition of products on the electrode was investigated with EC-AFM.

On basis of the new findings the reaction mechanism of the ORR in Ca^{2+} containing DMSO will be discussed.

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Pillar[5]arenes: comparison of electrochemical behavior in different organic solvent

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We have studied the electrochemical properties of dimethoxypillar[5]arene in two organic solvents, dichloromethane and acetonitrile.

Research based on host–guest chemistry has attracted considerable interest in supramolecular chemistry for many years. Over the last decade, not only in optical but also electrochemical sensing, macrocyclic hosts like cyclodextrins, calixarenes or crown ethers have been in the spotlight. However, recently, in 2008 Ogoshi[1][1] reported a new type of macrocyclic compounds called Pillar[n]arenes. Pillar[n]arenes consist of five or six hydroquinone units linked by methylene bridges in the para position. Their rigid, symmetrical and cylindrical structures as well as the ease of functionalization make them particularly attractive in comparison to many other host molecules. Host-guest complexation as well as structure properties of different pillar[n]arenes are mainly studied by spectroscopic techniques. Far less research has been carried out by voltammetric techniques. Since most of the pillar[n]arenes are dissolved in organic solvents, voltamerometric studies were performed mainly in dichloromethane[2][3] solution or with aqueous electrolytes[4] mixed with acetone.

The main goal of this work was to investigate the anodic voltammetric behavior of dimethoxypillar[5]arene using cyclic voltammetry and pulse techniques. The influence of different organic media - dichloromethane and acetonitrile in which we conducted our voltammetric experiments, on redox properties were studied. Discrepancy of redox reaction reversibility were compared using different scan rate and range of potentials. The proposed approach could provide better description of pillar[n]arenes voltammetric behavior and thus could be helpful in the understanding of the electron donor properties in supramolecular host–guest interactions.

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Acknowledgments

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Comparison of Photoelectrochemical Activities of Calcined and Uncalcined TiO_2 / $BiVO_4$ Photoanodes

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Among the various energy sources, hydrogen is considered as an efficient energy source which stands out due to its high energy per mass content, easy transportability and clean electricity generation. Furthermore, hydrogen production not only obtained from water splitting with solar light irradiation but also zero CO_2 emission to earth. A most of promising photoanode material TiO_2 has more advantage because of easy synthesis method with various surface morphology for photoelectrochemical hydrogen production [1, 2]. Herein, we introduced that one-dimensional, versatile TiO_2 with rutile phase structure was synthesized via hydrothermal method on conductive glass substrate (FTO) and then modified with $BiVO_4$ by electrochemical deposition and drop casting method. Fig. 1 shows Nyquist(a), Bode(b) and Phase angle-frequency(c) plots of electrodes. EIS measurement was carry out under a bias potential of 0.6 V to examine oxygen evolution reaction (OER) on electrode surface. It indicates that Uncal_TiO_2/$BiVO_4$ electrode is the smallest semi-circle in order to utmost photocatalytic response under solar irradiation compare to applied calcination on TiO_2. LSV result of electrodes display in Fig. 1 d. Uncal_TiO_2/$BiVO_4$ electrode demonstrates a high photo-current density at 1.0 V (0.474 mA cm^{-2}) in contrast to calcinated TiO_2 electrodes for photocatalytic hydrogen production under solar light. It suggests hindering rate of electron-hole recombination and improved photoelectrode separation.

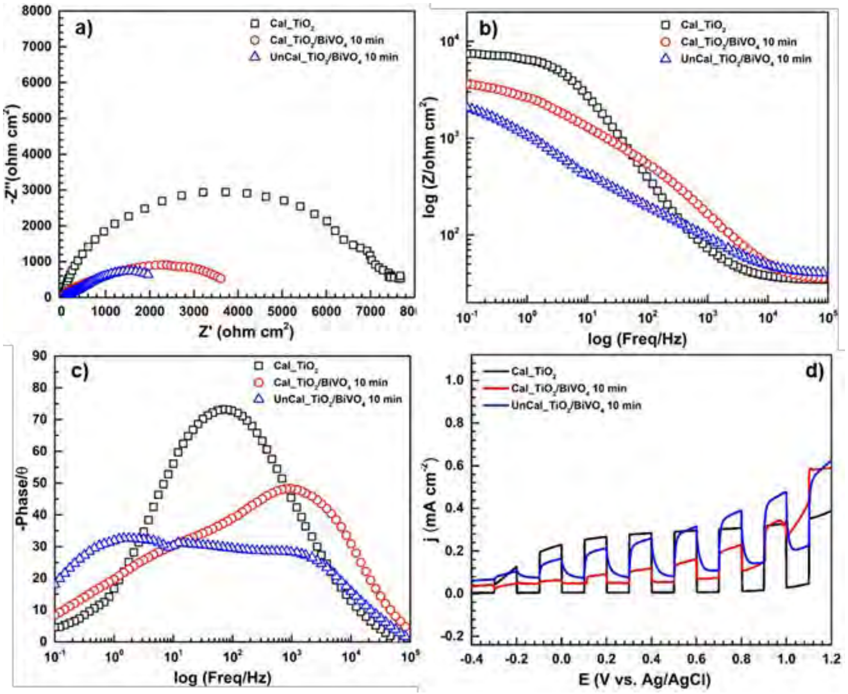

Fig. 1. Nyquist a), Bode b), phase angle-frequency c) and LSV d) graph of electrodes in 0.1 mM Na_2SO_3 electrolyte with 0.1 mM phosphate buffer.

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Electrochemical Study of The Effect of Aluminum Ions on The Stability and Performance of Cu-Based Catalysts in Atom Transfer Radical Polymerization in Organic Media

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Copper-based catalyst complexes played a critical role in the development of atom transfer radical polymerization (ATRP).[1] Among recently developed various advanced techniques, electrochemically mediated ATRP (*e*ATRP) proved to be a clean, robust and versatile method. The applied potential or current (E_{app} or I_{app}) determines the Cu^I/Cu^{II} ratio, allowing easy fine-tuning of reaction rate and polymerization control.

However, *e*ATRP is usually carried out in a divided cell with a separator that significantly increases the overall resistance. Also, Pt electrodes are often used. However, it has been shown that *e*ATRP can be successfully achieved on non-noble metals and also in undivided cells with Al anodes. In the latter cases, a significant challenge aroused due to the small amount of released metal cations. Indeed, it was observed that the presence of Al^{3+} in DMF strongly interferes with the catalytic system, drastically affecting the performance of *e*ATRP catalyzed by $[Cu^{II}Me_6TREN]^{2+}$.[2] However, the nature of the interference of Al^{3+} ions with Cu complexes was not investigated in depth. Here we report a detailed investigation on the effect of Al^{3+} on the performance of two of the most active and widely used ATRP catalysts, $[Cu^{II}Me_6TREN]^{2+}$ and $[Cu^{II}TPMA]^{2+}$, in DMF, DMSO, and MeCN.

These complexes have been previously used in *e*ATRP in both organic solvents and water.[2-5] In general, very stable Cu complexes with 1:1 Cu^{II} to ligand stoichiometry are formed.[6] Fig.- 1 illustrated the effect of Al^{3+} on the voltammetric behavior of $[Cu^{II}Me_6TREN]^{2+}$. When $C_{Al^{3+}}/C_L$=1.5 in DMF (Fig. 1a), two well-separated irreversible reduction peaks followed by an anodic stripping peak were observed in place of the reversible peak couple of $[Cu^{II}Me_6TREN]^{2+}$, which instead disappears. The presence of Al^{3+} caused dissociation of $[Cu^{II}L]^{2+}$ with release of Cu^{2+}, which is reduced to Cu^+ at less negative potential. Fast disproportionation of the latter to Cu^0 and Cu^{2+} and/or reduction at the electrode produced a deposit of metallic Cu on the GC electrode. Similar phenomena were observed also in DMSO and MeCN (Fig. 1b and c). Interestingly, the typical voltammetric pattern of $[Cu^{II}L]^{2+}$ could be restored by adding excess ligands. Conversely, the stability of $[Cu^{II}TPMA]^{2+}$ was affected by Al^{3+} only in MeCN.

The role of Al^{3+} was also investigated in *e*ATRP of butyl acrylate, providing results in agreement with the voltammetric analysis. In conclusion, this study, together with an ongoing work in water, provides useful guidelines for *e*ATRP in undivided cells with sacrificial Al anodes.

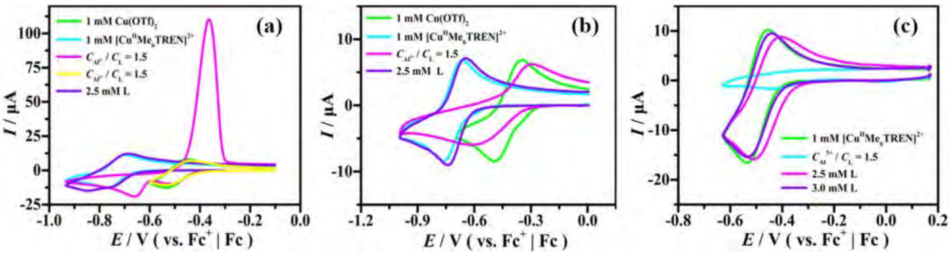

Fig. 1 CVs of 1 mM Cu $(OTf)_2$ in the presence of 1 mM Me_6TREN, 1.5 mM Al^{3+}, and excess Me_6TREN in (a) DMF, (b) DMSO, and (c) MeCN, recorded on a GC electrode at $\upsilon = 0.2\ V\cdot s^{-1}$.

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Modeling of Charge Transfer and Mass Transport at 3D Printed Composite Electrodes

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3D printing has been applied to every field of chemistry including electrochemistry. In recent years conductive composites containing different allotropes of carbon [1,2] or metals such as copper [3] have been used to manufacture 3D printed electrodes. For carbon nanotube-based composites it was recently demonstrated that after simple anodic activation procedure almost the whole surface of the electrode becomes electrochemically active (85 % relative area, further denoted as A_{EC}). On the other hand, current sensing atomic force microscopy imaging revealed that only 33% of the electrode surface is electrically conductive (A_{CON}). [1] To explore relationship between A_{EC} and A_{CON} we performed finite-element-method numerical simulations of cyclovoltammetric experiments with the electroactive probe in the electrolyte and composite electrodes. Simulations considered model 2D geometries and were performed in program COMSOL Multiphysics®. [4] In the electrolyte phase a continuity equation is formulated for both (oxidized and reduced) forms of the probe. The charge transfer at the electrode/electrolyte interface is formulated as Butler-Volmer kinetic expressions introduced as source/sink terms of the electrode boundary condition of continuity equations. Results (Figure 1) indicate that the non-linear diffusion is of great significance at the interface of electrolyte and composite electrodes. The simulated cyclovoltammetric response of the electroactive probe at the composite electrode with A_{CON} = 33 % (corresponding to the electrode surface shown Figure 1B) leads to A_{EC} = 98 %. This value is comparable to experimental value obtained at the electrode 3D printed from this composite (A_{EC} = 85 %).

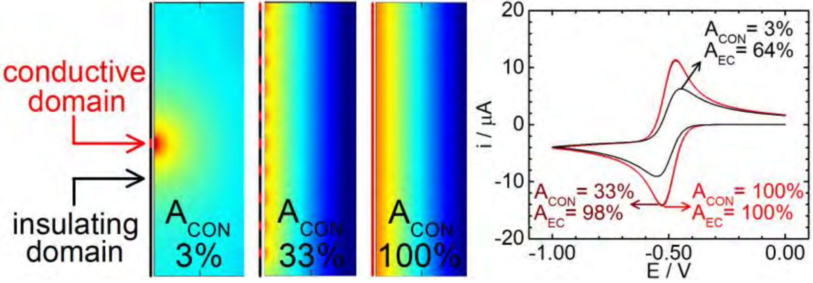

Fig. 1 COMSOL simulations. (A) Concentration profiles of the reaction product generated at composite electrodes with A_{CON} values of 3 to 100 %. (B) Corresponding simulated voltammograms.

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Structure and Stability of Cu Single Crystal Electrodes in Phosphate Electrolyte studied by In-situ Surface X-ray Diffraction

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Electrochemical reduction of CO_2 into carbon-based fuels has received great attention due its importance as source of renewable energy. Copper and copper oxide electrodes are well known to electrochemically convert CO_2 to a range of products. The selectivity is associated to the species adsorbed on the surface and/or its crystallographic orientation [1]. For example, methane is the dominant product on Cu(111), whilst ethylene is favoured on Cu(001) [2].

Surface x-ray diffraction (SXRD) can be used to study Cu electrodes in electrochemical environment and correlates the changes in the atomic structure with the redox reactions. In this work in-situ SXRD studies are presented on Cu(111) and Cu(001) electrodes in a neutral phosphate buffered electrolyte (pH 8). Strong dependence in the morphology and stability of the Cu(111) surface during the potential cycling arises from the preparation method and history of the electrode. The phosphate adsorption and deprotonation of the (di)-hydrogen phosphate can lead a fully reversible adsorption process of oxygenated species for a smooth and defect free surface.

However, in the presence of defects on the electrode surface, the formation of a mixed copper-oxygen layer is accompanied by irreversible changes on the surface morphology due to a 3D Cu growth mechanism [3]. Results for Cu(001) oriented electrodes in the same electrolyte suggest a potential dependent roughening and facet formation. In the presence of defects and for prolonged potential changes the formation of Cu(111) terminated islands is observed.

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Electrical Conductivity of Films Formed by Few-Layer Graphene Structures

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The mass production of high-quality graphene is important for its application in next-generation electronics, composite materials, energy storage devices, humidity sensors and development of platinum group metals free catalysts of oxygen reduction reaction (ORR). Therefore, determination of conductivity of films formed by graphene structures is of both fundamental and applied importance. In this study, we propose a simple and effective method to estimate the resistance of films formed by few-layer graphene structures obtained by plasma-assisted electrochemical exfoliation of graphite electrodes in 0.3–1 M Na_2SO_4 solutions [1]. The analysis of the influence of humidity and the nature of solvent on the conductivity of FLGS films was carried out.

Synthesized graphene-like structures are particles with a wide distribution of lateral size,which varies from 60 to 550 nm. The thickness of FLGS flakes was estimated at 2–4 nm; the thickness of FLGS films is 200–300 nm. According to X-ray photoelectron spectroscopy, the content of O and S is 18.8 and 1.3 at.% for c-FLGS and 23.8 and 4.1 at.% for a-FLGS.

In a dry atmosphere, a current observed for FLGS films is determined by their electronic conductivity. An increase in the relative humidity always leads to a sharp decrease in the current and a subsequent gradual decrease in its value. The observed decrease in conductivity of FLGS films in a humid atmosphere is associated with the shielding of FLGS flakes by a film of water. Returning a sample to a dry atmosphere leads to an abrupt growth and further slow recovery of the current values. Probably, the reverse process proceeds much slower, since the rate of water molecules removal and restoration of electrical contacts between FLGS flakes is less than the rate of formation of water film around FLGS particles. The electronic conductivity of films in a dry atmosphere could be a qualitative criterion for a small degree of functionalization of FLGS surface. However, in our case, the oxygen content in FLGS is sufficiently high and electronic conductivity should be explained by the fact that functional groups are mainly concentrated at the edges of graphene planes.

We observed a change in the conductivity of FLGS films in vapors of various solvents: heptane, CCl_4, ethanol and water. Despite high saturation vapor pressure, in the atmosphere of non-polar solvents (heptane, CCl_4), the conductivity of FLGS films is higher than that in the case of ethanol and water. Evidendly, high concentration of hydrophilic groups at the edges of graphene planes contributes to faster wetting of flakes and to more intensive diffusion of polar molecules into the film.

Thus, the conductivity of FLGS films can be controlled by external conditions, i.e. by increasing or decreasing the vapor pressure of various solvents. With the increase in vapor pressure, the molecules of polar solvents diffuse into FLGS film. It causes a lessening of the number of contacts between FLGS flakes and, consequently, the electric current decreases. Moreover, established influence of chemical nature of solvent on the electrical conductivity of FLGS films is due to the hydrophilic nature of synthesized FLGS particles.

The study was performed in accordance with the State Assignment (state registration No 0089-2019-0007). The work has been performed using the equipment of the Multi-User Analytical Center of IPCP RAS.

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Proton Conductivity of Graphene Oxide and Nafion Films: Effect of Dry Charged Battery

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After separation of individual graphene sheets in 2004, the world's interest in graphene and graphene-like materials increased dramatically. Graphene oxides (GO) were initially considered as a source product for the production of graphene but are currently being actively studied to be used in various materials and devices. Materials with proton conductivity are used in various devices: fuel cells; electrolysis cells; electrochemical sensors; electrochemical reactors, electrochromic devices. Proton transport is observed in biological systems. In the dry state GO is an insulator, and in a humid atmosphere GO demonstrates proton conductivity. As a proton conductor the GO has various applications: humidity sensor, a separator in a supercapacitor, also in a field-effect transistor, and nanocomposite membranes. The proton conductive Nafion is widely used in fuel cells as membranes, it possesses high proton conductivity and the ability to control its swelling in water. In the present work the effect of charge accumulation in film was shown to be common to proton conductors. The effect of charge accumulation and conservation was studied using the example of proton conductors - Nafion and GO films

GO and Nafion films are typical proton conductors in water vapor and their conductivity depends on the humidity of the environment. The charging curve (curves 1 in Fig. 1) has a characteristic feature with a maximum in the initial period and a gradual decrease in current to a stationary value in the course of measurement. Such behavior of the current can be explained by vacancies filling with protons from the negative electrode and electrons from the positive electrode. The current decrease on curve 1 is comparable with the discharge current on curve 2 (Fig. 1). The amount of accumulated charge (discharge current) is proportional to the charging current. In this case, their difference (the sum of curves 1 and 2) corresponds to the stationary current in the cell, as can be seen from curve 3 in Fig. 1.

In the case of GO at a voltage of 400 mV and a film thickness of about 400 nm, the charge is about 10^{-6} C. The maximum charge value is limited by the concentration of traps in GO (OH groups) and can theoretically be ~ 10^{-2} C. In a dry atmosphere, the charge is maintained even when the voltage is applied to the electrodes - the current occurs only in a humid atmosphere. The observed behavior of the current in the films of GO and Nafion is similar to a charged capacitor, this process can be compared with the behavior of a dry-charged battery, unlike liquid batteries, where the charge is stored as a chemical compound accumulated during charging.

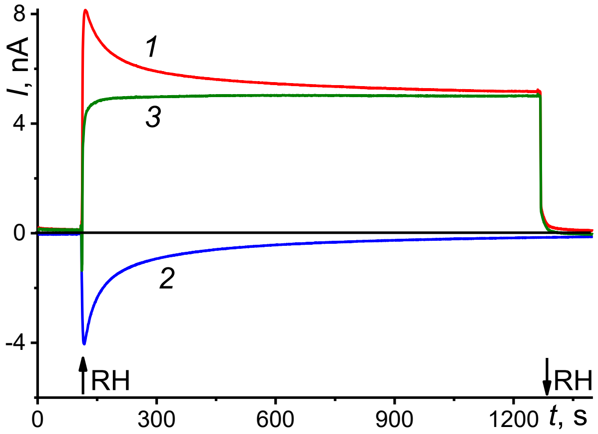

Fig. 1. *1* – The kinetics of charge accumulation in GO film at RH = 75%, U = 0.4 V. *2* – Process of GO film discharge at RH = 75%, U = 0 V.
3 – The sum of curves 1 and 2.

For the first time, the possibility of accumulation and storage of charge in films of typical proton conductors was shown experimentally using GO and Nafion films. The amount of charge accumulation depends on the humidity of the environment. In a dry atmosphere the accumulated charge can be stored for up to several days. Accumulation of charge occurs directly in GO or Nafion film, which significantly distinguishes proton conductors from electric capacitors and liquid batteries.

The study was performed in accordance with the State Assignment (state registration No 0089-2019-0012). The work has been performed using the equipment of the Multi-User Analytical Center of IPCP RAS.

Assessment of Antioxidant Activity of Some Chlorogenic Acids by an Electrochemical DNA-based Biosensor

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An electrochemical DNA-based biosensor, dsDNA/SWCNT-COOH/SPCE, was applied for the first time to assessment of antioxidant activity of six chlorogenic acids (CGAs) After the incubation of the electrochemical biosensor in the mixture of a DNA cleavage agent created by the Fenton type reaction, the degree of dsDNA degradation was determined using cyclic voltammetry (CV) of the redox indicator $[Fe(CN)_6]^{3-/4-}$. The normalized biosensor responses observed from CVs (ΔI_{rel} and $\Delta(\Delta E_{p,\ rel})$) were used to express the antioxidant activity of CGAs. The results showed that addition of CGAs in the cleavage agent significantly reduces the degree of DNA degradation and the antioxidative activity decreases in order caffeic acid, CFA, > caffeoylquinic acids, CQAs, > dicaffeoylquinic acids, diCQAs, exposure the relative portion of survived DNA of about 71 %, 70 % and 69%.

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Electrochemical Imaging of Biomarkers for Oral Cancer Staging

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Each year, approximately 450,000 new cases are reported with oral or oropharyngeal cancer worldwide. Despite their high incidence, oral cancers are often neglected at the first stage, resulting in cancer metastasis with high mortality rate, especially for men. Conventional methods for diagnosis of oral cancer rely on the visual inspection and biopsy. However, it may lead to misdiagnosis or delayed diagnosis because of insufficient information. Therefore, it is important to develop a novel tool for the detection of oral cancer at an initial stage itself.

Electrochemical screening methods have shown to be very promising for the rapid, sensitive, and cost-effective detection of oral cancer biomarkers.[1] To enhance the resolution of the electrochemical imaging, we employ the concept of image fusion, with the image obtained by scanning electrochemical microscopy (SECM) and optical microscopy. Through the prediction of the presence of biomarkers in tissue area, the fused image can provide a more accurate description of the biomarker distribution of the oral cancer slices. For the purpose of investigating the distribution of IL-6 protein, a biomarker of oral cancer, in different cancer stages, we use SECM to image tissue sections and fused it with H&E stain images obtained by optical microscope. SECM is a scanning probe technique that is composed of three electrode system and soft probe can scan closely over a sample surface. The primary antibody and secondary antibody labeled with horse radish peroxidase (HRP) were applied to reveal the locations of IL-6 on the samples. Then, the cancer sections were immersed in electrolytes containing FcMeOH and H_2O_2. The $FcMeOH^+$ ions were generated from the catalytic reaction of HRP, and hence, the Faradaic current signals from the reduction of $FcMeOH^+$ can be recorded through the scanning of SECM probe. Due to the fusion of SECM with H&E stain, IL-6 distribution patterns in cancers with different stages can be analyzed precisely. We discovered that in stage III of oral cancer, the IL-6 expression level is the highest as compared to the normal tissue and cancer tissue at earlier stages.

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Electrochemical dual biosensor platform for the early diagnosis of prostate cancer

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The early diagnosis of cancer is decisive for the survival of patients. However, traditional protein tumor markers do not always exhibit the sensitivity and selectivity required in clinical diagnostics applications. For this reason, current trends search for specific biomarkers with clinical validity and highly sensitive detection methods. Recent progress in modern biology has revealed that the proportion of DNA that encodes proteins represents only 2% of the human genome, so the vast majority is transcribed into the form of non-coding RNAs. Among the latter, long non-coding RNAs (lncRNAs) i.e. transcripts with length above 200 nucleotides, make up a large group that has aroused special interest due to their participation in a wide range of biological processes, thus freeing themselves of their initial name of "junk RNA". Altered expression levels of certain lncRNAs in human body fluids have been recently related to different diseases including cancer, turning them into potential non-invasive biomarkers (liquid biopsy).[1][2] Among them, prostate cancer antigen-3 or PCA3 is the only one so far approved by the US-FDA as a urinary marker for prostate cancer diagnosis. In fact, PCA3 is a good alternative to traditional serum PSA able to distinguish between aggressive and indolent tumours.[3][4] However, to exclude any nonspecific variation, levels of PCA3 should be normalized with an internal RNA control of stable expression, which demands the development of multiplex tests.

In this work we report a sandwich-type hybridization assay for the detection of the urinary biomarker PCA3. To overcome the challenge of the long size and internal secondary structure of this transcript, as well as its low abundance, we have proposed the use of multiple fluorescein-tagged hybridization assistant probes to favour the selective capture onto the sensing platform, while incorporating multiple redox enzymes per target molecule, via fluorescein-antifluorescein interaction. This strategy enabled on-surface quantification with an enhanced sensitivity and a wider range of linear response. An equivalent approach was also designed and developed for the detection of PSA mRNA, selected as endogenous control for normalization, because it is not up-regulated in cancer. Both optimized genosensors were successfully integrated into the same sensing platform for simultaneous assessment of PCA3 and PSA RNA levels. The usefulness of this multiplex platform was demonstrated by analysing total RNA extracts from the prostate cancer cell line LNCaP.

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Electroactive Organically Modified Mesoporous Silicates on Graphene-Graphite 3D Architectures Operating with Electron-Hopping for High Rate Energy Storage

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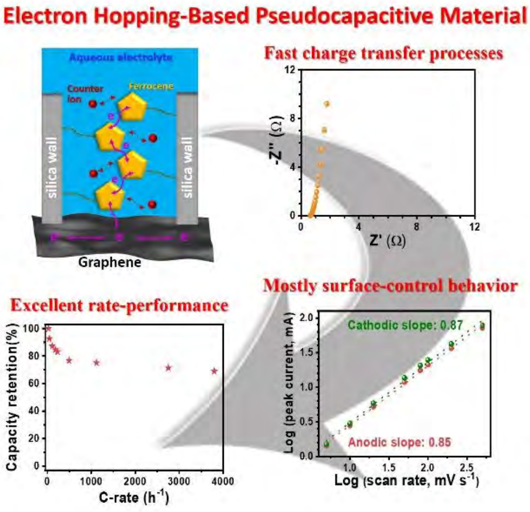
The ever-growing energy demand calls for energy storage devices with both high energy and power density. In contrast to electrical double-layer capacitors, the faradic pseudocapacitors can gain much higher energy density by involving faradic reactions, but the slow reaction rate severely restricts their power outputs. Here, a pseudo-capacitive material operating with electron-hopping as the charge transfer mechanism is generated onto a high surface area graphene current collector to study its interest in delivering fast redox reactions over a large-scale (contrary to monolayer-based electroactive systems). The extensive assembly of fixed redox molecules is achieved by anchoring ferrocene moieties onto the surface of graphene-supported mesoporous silica film and various physico-chemical techniques are used to characterize the resulting composite material. The obtained EG@Fc-MS electrode (ferrocene functionalized silica film coated onto electro-exfoliated graphene) can deliver a specific capacity of 196 mC cm^{-2} (326 mF cm^{-2}) at a current density of 2 mA cm^{-2} and a 69% capacity retention even at 3800 C, which is much better than the traditional faradic materials. The electrochemical analyses reveal the energy storage behavior of EG@Fc-MS is a fast surface-controlled redox process with the time constants τ_0 of 0.78 s due to the low resistance of charge transfer (no obvious semi-circle in Nyquist plot) and fast counter-ions compensation rate (diffusion coefficient ~1.9×10^{-5} cm^2/s). The electrode can be assembled into an asymmetric device which exhibits excellent cycling stability (no noticeable fading after 10 000 cycles) and competitive energy densities (respectively 17.7 or 9.2 µWh cm^{-2} at power densities of 0.53 or 13.7 mW cm^{-2}). These results open up new opportunities for pseudocapacitive materials based on electroactive inorganic frameworks bearing surface-tethered molecular redox sites with high energy storage capability.



Redox Properties of Electrophilic Fatty Acids

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A new class of lipidic signaling molecules known as nitro-fatty acids (NO_2-FAs) has been recently identified. NO_2-FAs possess unique electrophilic properties affecting enzyme activity regulation, the modulation of inflammation and various cellular responses in a broad spectrum of pathologies[1]. Because of their tissue-protective and anti-inflammatory properties, synthetic analogs of these species are involved in clinical evaluations as new drug candidates for the treatment of renal and pulmonary diseases etc.

In this study, we focused on an evaluation of the redox properties of nitro-oleic acid (NO_2-OA), conjugated nitro-linoleic acid (NO_2-cLA) and nitro-linoleic acid (LNO_2) using cyclic voltammetry and constant-current chronopotentiometric stripping (CPS) analysis. Nitroalkenes are stable in free and/or esterified form in hydrophobic micellar, lipoprotein, or membrane environments. Based on the reduction signal of the nitro group at a potential of around -0.8 V (vs. Ag/AgCl) at pH 7.4, the reactivity and stability of NO_2-FAs and NO_2-oleoyl-glycerol were studied[2]. EPR and fluorescence probe DAF-2 were used to evaluate its ability to release NO·.

The key mechanism of NO_2-FAs signaling actions is based on the post-translational modification of proteins. Electrophilic compounds mainly react with the -SH groups (Cys residues) of a variety of biological nucleophiles through Michael's addition reaction (Fig. 1). In our study we also focused on the interaction of NO_2-FAs with basic amino acid residues by CPS analysis. In a single CPS scan we can observe the reduction peak of NO_2-FAs at a potential of around -0.8 V and the peak H related to electrocatalytic process in which proton-donating amino acid residues (Cys, His, Lys and Arg) are involved. Depending on the decrease in both reduction peaks, the interactions of NO_2-FAs with the protein were monitored. Mass spectrometry (peptide mapping) and spectrophotometric (Ellman's and ninhydrin) methods were utilized to evaluate the formation of Michael's adducts.

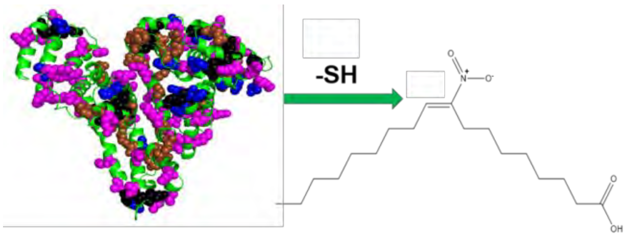

Fig. 1. Schematic representation of interaction of 9-nitro-oleic acid with human serum albumin. In the model of human serum albumin, electroactive amino acid residues (His-blue, Arg-brown, Cys-black and Lys-purple) are highlighted.

The data presented here are the first mechanistic view of the redox properties, reactivity and stability of NO_2-FAs, and could be used in further molecular studies focusing on other electrophiles with high biological relevance.

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Physical and Electrochemical Studies of Carbon Coated $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ Cathode Material in Lithium Battery Configuration

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The nickel-rich NMC ($LiNi_xMn_yCo_zO_2$, x+y+z=1; where, x≥0.6) is regarded as promising cathode active material for future Li-ion batteries due to their ability to deliver high specific capacities. However, their capabilities are limited by the unwanted side reactions with the electrolyte leading to decomposition on the surface of the particles at high voltage (> 4.2 V vs. Li^+/Li). This also leads to surface degradation and limited cycling performance [1]. Surface coating is a predominant strategy to minimize side reactions that occur on the surface preventing material degradation [2].Due to high electronic conductivity and stability of carbon against electrolytes at higher voltages, this study presents for the first time a carbon-coated $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$(NMC622/C) material using the approach of polymerising furfuryl alcohol monomers on the surface of NMC particles followed by a carbonization step. This simple mixing approach for the coating process opens up the possibility of an easy implementation in industrial processes. Numerous analytical techniques were performed to characterize the coated materials, i.e. Thermogravimetric Analysis (TGA) to understand the kinetics during carbonisation, in-situ High-Temperature X-Ray Diffraction (HT-XRD) to monitor the phase changes, Scanning and Transmission Electron Microscopy (SEM & TEM) were used to observe the morphology of the particle. Fourier-Transform Infrared (FT-IR) spectroscopy to observe the presence of polymerisation and the carbon in the sample, CHNS(O) analysis to quantify the amount of carbon in the sample after the heat treatment step. Furthermore, electrochemical; analysis such as cyclic voltammetry, charge-discharge and rate capability tests were carried out to investigate the impact of the carbon coating on the electrochemical performance and structure stability of the material. The results from the XRD show no phase change in the sample after the calcination, SEM and TEM show the homogenous coating of the carbon on top of the NMC and FT-IR shows the presence of the carbon bonds on the calcined samples, TGA results show the decomposition of the polymer ~230°C and formation of carbon. Further, the rate capability test shows ~15% improvement in the capacity of the coated samples.

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Insights into Carbon-Carbon Bond Formation on Silver Surfaces

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The electro-valorization of carbon dioxide has been investigated for decades,[1] with fairly recent renewed interest and investments sparked by its detrimental environmental effects. Disregarding current catalyst performance and economic viability, the study of the formation of liquid carbonic species and carbon-containing platform molecules is an important and interesting scientific endeavor due to the industrialized world's widespread employment and reliance on such molecules. Its importance is further substantiated by the fact that the current source of these chemicals (i.e. oil) is an exhaustible commodity that is distributed unequally globally, as opposed to CO_2, H_2O and electricity, which are readily available.

Regarding the electro-reduction of CO_2, copper catalysts have long enjoyed the limelight due to their capability of forming C-C coupled products such as ethanol and ethylene with somewhat reasonable faradaic efficiencies.[2,3] However, notwithstanding the enormous amounts of effort invested in studying this system,[4] selectivity and activity for the production of C_{2+} species still remain an obstruction to industrial viability. In part, the non-selectivity of the reaction can be explained mechanistically: the proposed pathways for different carbon-coupled products share many intermediates before eventually bifurcating at the later stages.[4-6]

As the pathway depends predominantly on the catalyst's attributes and local surface structure, the selectivity issues of copper catalysts are rather an inherent property of the system. On this account, we decided to step away from copper catalysis and investigate a different catalytic system capable of forming C_{2+} species: Ag.[7] Silver is part of a small group of catalysts known to date that are capable of producing carbon-coupled products,[7-10] and was chosen on the basis of a theoretical study wherein it was calculated that (thermodynamically speaking) silver surfaces should be superior to copper in producing ethanol.[11] Thus, this study concerns itself with investigating the mechanism of C-C bond formation on silver.

Because of the unfavorable adsorption energy of carbon monoxide on silver surfaces,[12] the CO reduction reaction (CORR) was studied at a series of elevated CO pressures so as to increase the fractional coverage of CO_{ads}. This enhances the likelihood of the reaction between two adsorbed carbon (e.g., monoxide) species, which is important for the C-C coupling step(s) that is (are) fundamental in producing C_{2+} species. The reaction was carried out on a GDE to maximize surface area and thereby product formation, and conducted in alkaline electrolyte to negate any local pH effects.

It was observed that at pressures between 10-60 barg, CO can be further reduced on metallic silver to yield methane (gaseous) and methanol, ethanol, n-propanol, acetate and ethylene glycol (liquid). Notably, ethylene was not observed as a product. By increasing the pressure, faradaic efficiency towards CO reduction (vs. HER) at the same applied potentials was found to increase, with the sum of C_{2+} product faradaic efficiency reaching ~6% at 60 barg of CO at an applied potential of -2 V_{RHE} (non-IR corrected). As is evident from the product distribution, the silver surface is capable of breaking C-O bonds. But, the absence of ethylene formation indicates that the final C-O bond breaking step appears to be suppressed on silver, which is in agreement with computational predictions.[11]

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Hierarchically Porous Mn_2O-Inlaid Carbon Hybrids for Lithium-Sulfur Batteries

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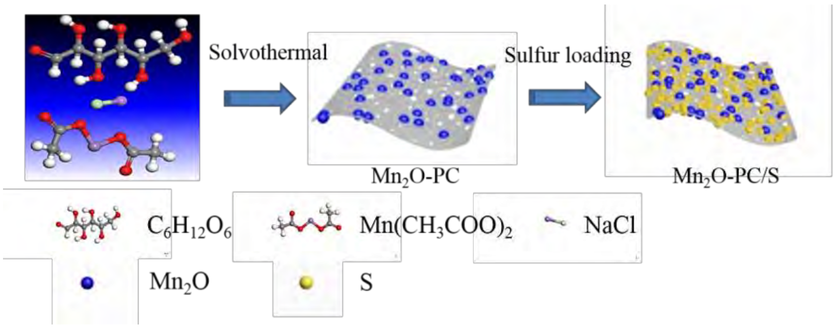
Abstract:

Lithium-sulfur batteries possess tremendous prospect in the future energy evolution, despite facing some tough challenges on the road. Carbon coated low-valence state polar metal oxide Mn_2O rarely reported, which owning a hierarchical porous nanosheet in figure 1a benefit to alleviate the shuttle effect of lithium-sulfur batteries and immobilize the soluble polysulfide in the process of galvanostatic charge/discharge to improve the electrochemical property by chemisorption and physical limitation. And the composite synthesized by simple hydrothermal and pyrolysis methods in the scheme 1. The mode of Mn_2O-PC/S-800 established reveals 1384 mAh g^{-1} at 0.2 C in the initial discharge which closes to the theoretical specific capacity 1675 mAh g^{-1} and high-retention capacity of 593 mAh g^{-1} after 200 cycles in figure 1b.

Keywords: lithium-sulfur batteries, chemisorption, carbon coated, Mn_2O, low -valence state



Scheme 1. Schematic illustration the synthesis process of Mn_2O-PC/S.

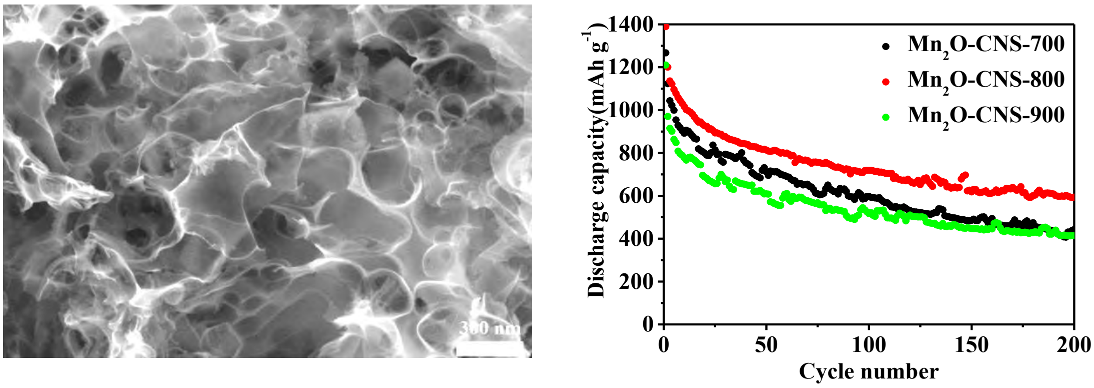


Figure 1. (a) The FESEM images of Mn_2O-PC: (b) Cycling performance of Mn_2O-PC obtained at different temperatures after sulfur melted.

MoS_2-TiO_2-rGO Composite as Electrode Material for Na-Ion Capacitor Device For Durable Cycle Performance

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Ever growing demand of portable electronic devices and EV, which requires Li based storage devices leads to the depletion of Li reserves in the earth. With practically inexhaustible and less cost, Sodium could replace the Li as charge carriers in electrochemical storage devices. Na-ion capacitor is one type of hybrid storage device which delivers high energy density, high power density and long-life span. In present work, MoS_2-TiO_2-rGO (MTG) was synthesized composite using hydrothermal route. MoS_2 possesses layered structure where Mo atoms are sandwiched between two planes of S atoms and it leads to higher charge diffusion at layer interfaces. Large charge accumulation is possible due to higher surface area of MoS_2. Further, MoS_2 was composited with TiO_2 and reduced graphene oxide (rGO) for following reasons: (a) TiO_2 has large ion diffusion length and improved electron mobility due to presence of Ti^{3+} and Ti^{4+} at the surface, which confirmed by XPS. (b) Graphene oxide has excellent electrical, mechanical properties and power handling capability. The device was fabricated using coin cell with non-aqueous electrolyte, $NaClO_4$ in DEC/PC (diethylene carbonate/propylene carbonate). Both anode and cathode electrodes were coated with MTG by Doctors blade method. Cyclic voltammetry was performed for the device at different scan rates, which shown in the figure 1a. The CV results shows the rectangular shape and symmetrical pattern discloses better suitability of composite material for electrochemical storage devices. The charge-discharge profile of the MTG device is shown in the figure 1b at different current densities such as 1 Ag^{-1}, 1.25 Ag^{-1}, 1.5 Ag^{-1}, 1.75 Ag^{-1} and 2 Ag^{-1}. Symmetric charge and discharge curves show good capacitive storage behavior of the device. Energy density of the device is about 17 $KW\text{-}hkg^{-1}$ and power density stands at 1300 $W\text{-}hkg^{-1}$. Excellent cycle stability was exhibited by the device for 10000 cycles at the current density of $2Ag^{-1}$ without any degradation in efficiency, which is shown in the figure 1c. The remarkable cyclic stability is attributed from positive synergetic effect from MoS_2, rGO and TiO_2. The presence of rGO is not only ensured the stability electrode but also improved the electrical conductivity of MoS_2 and prevented the agglomeration. The interfacial charge transfer between individual elements in the composite improved the intercalation and ion transfer. This work gives more insights about the synergetic effect of MTG composites in cycle stability which is very crucial for practical applications. In best of our knowledge, it is the first time in reporting MTG for Na-ion capacitor

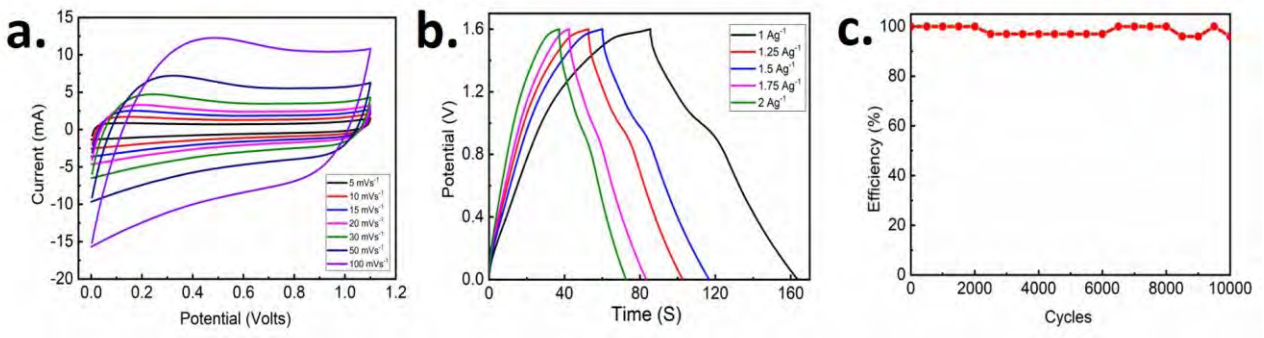

Figure 1. Electrochemical characterization of MTG device a) Cyclic voltammetry b) Charge-discharge profile c) Cycle life

Low-Overpotential Li-O_2 Battery with Ru nanoparticles in-situ Formed on Binder-free Carbon Paper

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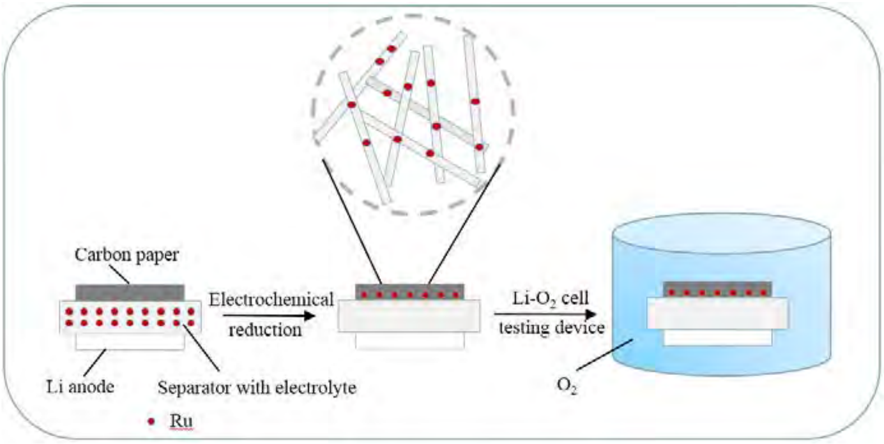
Today, for numerous next-generation energy storage devices[1], non-aqueous Li-O_2 battery has triggered worldwide attention due to its ultrahigh energy density (about 3500Wh/kg)[2]. But one of the problems is the sluggish redox kinetics caused by insoluble and insulating Li_2O_2[3], thus developing high-efficiency electrochemical catalysts is necessary for Li-O_2 battery. Hence, we achieve Ru nanoparticles catalyst that in-situ generate on carbon paper without binder by electrochemical method. Firstly, we prepare electrolyte containing Ru^{3+} to assemble coin-type cell with carbon paper, the constant-current discharging of cell exhibits a steady platform corresponding to "$Ru^{3+} \rightarrow Ru$", Ru nanoparticles uniformly coat on 3D space network skeletons of carbon paper. We find that the binder-free carbon paper with Ru nanoparticles in Li-O_2 cell shows remarkable ORR and OER low-overpotential (0.15 V and 0.2 V, respectively). The work presents a new design of a binder-free O_2 electrode for Li-O_2 battery, which gives an insight into the improvement about the preparation of in-situ catalysts.



Scheme 1. Illustration of the preparation of catalysts and battery testing.

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Exploring dynamic interactions of single nanoparticles at interfaces for surface-confined electrochemical behavior and size measurement

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Single-entity electrochemistry has attracted increasing attention not only for its extremely high sensitivity but also for the insight that it offers with respect to individual direct electron transfer that is masked in ensemble-averaged measurements.[1] Over the past several decades, electrochemical measurements of individual entities, including nanoparticles (NPs), cells, molecules, and atoms, have been achieved conveniently with the use of stochastic collision measurement at a ultramicroelectrode (UME) or nanoelectrode. Significant advances have been made in the analysis of the dynamic electrochemical behaviors of individual entities.[2–4] Although the combination of stochastic collision electrochemistry with scanned nanoprobe microscopies or optical-based techniques was introduced as a new tool for real-time analysis of the electrochemical reaction mechanism/kinetics of individual NPs with high spatial and temporal resolution, it remains an open and challenging issue to elucidate how nanoscale particles interact with an electrode interface to clearly understand the dynamic electrochemical processes of such particles. Here, using first-principle density functional theory (DFT) calculations, we study the adsorption-energy scaling relations by examining NPs on two different UME surfaces. This allows us to semi-quantitatively predict the adsorptive interaction effect of NPs on UME interfaces and helped helps in identifying the dynamic electrochemical nature of single NPs during the stochastic collision process. Based on the theoretical predictions, we explored the interaction-modulated electrochemical oxidation behavior of individual AgNPs, producing significantly distinguished current traces (Fig. 1).[5] By attempting to suppress the stochastic path of AgNPs and control their motion in an alkaline media, we observed the complete oxidation of the AgNPs with different diameters of 10, 18, 34, 55, 65 and 75 nm, and successfully realized the in-situ size discrimination of AgNP mixtures with multi-parameter analysis using the stochastic collision electrochemistry.

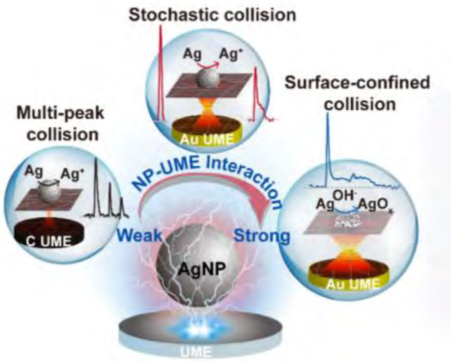

Figure 1. Interaction-modulated dynamic electrochemical behaviors of single NPs.

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Durability of nickel electrode coated with manganese-based mixed metal oxide for alkaline water electrolysis

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Introduction

Alkaline water electrolysis (AWE) has attracted much attention for hydrogen production from renewable energy. One of the most important issues in water electrolysis is to prevent degradation of electrodes under fluctuation of power from renewable energy. Nickel is well known as a good AWE anode; however, frequent start/stop simultaneously causes its corrosion due to oxidation and reduction.1) It has been reported that the coating of nickel with conductive metal oxides improves durability, whereas activity was somewhat lowered.2) Manganese-based mixed metal oxides (MMMO) have high oxygen evolution reaction (OER) activity and are used as secondary battery electrodes with high cycle stability; thus, MMMO is expect to have both high activity and durability. Here, the activity and durability of MMMO-coated nickel electrode were investigated under potential cycling test.

Experimental

Catalyst deposition: a nickel plate was etched 10 min in 20 wt. % HCl solution at 90 °C. The plate was then vertically immersed into 0.2 mM $KMnO_4$ aq. (50 mL) and hydrothermally reacted at 180℃ for 20 h. This coated electrode was again immersed into 0.2 mM $CoCl_2$ aq. (50 mL) and hydrothermally reacted at 130℃ for 3 h, followed by calcinated at 500 ℃ for 1 h. The obtained nickel plate covered with Co-Mn mixed metal oxide is denoted CMN130.

Electrochemical measurement : the working, counter, and reference electrodes were CMN130, Ni coil, and reversible hydrogen electrode (RHE), respectively. 1.0 M KOH was used as an electrolyte. Cyclic voltammetry (CV) was performed at 50 mV s^{-1} between 0.5 and 1.8 V vs. RHE for 100 cycles as pretreatment. The durability test was performed by repeating the following processes for 20 times. CV at 5 mV s^{-1} between 0.5 and 1.8 V vs. RHE for 2 cycles, CV at 500 mV s–1 in the same range for 1000 cycles, and AC impedance at 1.6 V vs. RHE to correct *iR*.

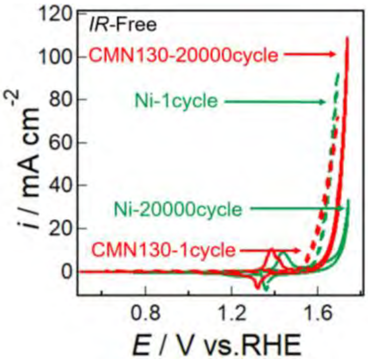

Fig.1 CV curves of Ni and CMN-coated Ni at 1st and 20000th cycles.

Results and discussion

The formation of δ-MnO_2 and Co-Mn-O spinel oxide at the first and second hydrothermal reactions, respectively, was confirmed by XRD. The δ-MnO_2 consisted of platy particles, and the spinel layer consisted of nanoparticles. The polarization curves of CMN130 and nickel presented the overpotential (η) 276 and 24 mV, respectively, at 10 mAcm^{-2}, showing that CMN130 is more active for OER than the nickel (Fig. 1).

In the durability test (Fig. 2), nickel was activated at 1000th–2000th cycles, whereas η significantly increased after the 3000th cycle. On the other hand, CMN130 showed lower overpotential compared to Ni in every cycle. Almost no degradation was observed up to the 6000th cycle. η increased after the cycle, though η is always lower than those of nickel at the same cycle. At the 20000th cycle, the redox peaks due to Co(II/III) t 1.38 V vs. RHE and Ni(II/III) at 1.41 V vs. RHE were observed for CMN130, implying that the nickel surface is exposed by partial detachment of the MMMO layer. In conclusion MMMO made by hydrothermal reaction showed good stability and durability under potential fluctuations.

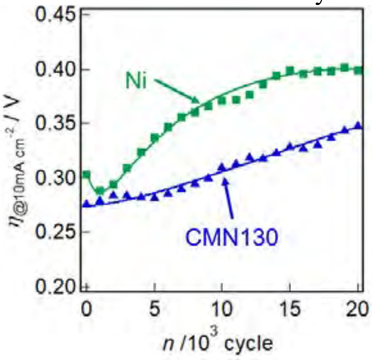

Fig.2 OER overpotential as a function of durability test cycles.

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Distribution of relaxation times: A tool for measuring oxygen transport resistivity in the catalyst layer of a low-Pt PEM fuel cell

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Oxygen transport ohmic resistivity R_{ox} in a low--Pt PEM fuel cell has been determined using two methods. The first one is fitting of our recent physics--based impedance model [1] to the experimental impedance spectra. The second method is calculation of distribution of relaxation times (DRT) using the same experimental spectra. Comparison of the two methods shows that the DRT peak with the characteristic frequency on the order of 500 to 1000 Hz describes oxygen transport in the open pore and in Nafion film covering Pt/C agglomerates in the catalyst layer. The resistivities R_{ox} calculated by the two methods agree well. This result makes it possible using experimental impedance spectroscopy and DRT for routine measurements of R_{ox} in low-Pt PEMFCs.

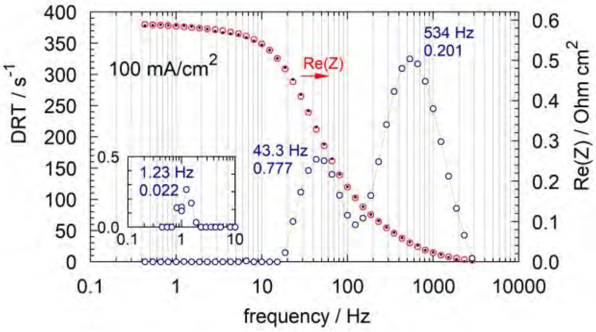

Figure 1. DRT of a low-Pt PEMFC (blue open circles) and the real part of cell impedance: measured (solid points) and reconstructed from DRT (red open circles).

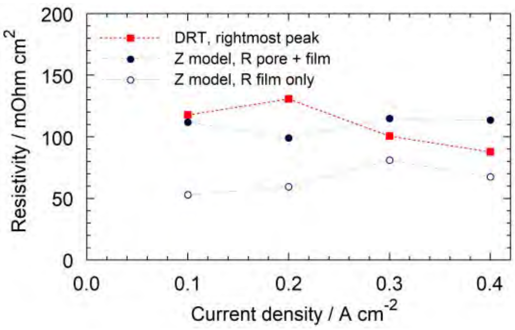

Figure 2. Oxygen transport resistivities determined from DRT (red squares) and from impedance model fitted to the spectra.

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Interface Engineering and Performance Improvement of Solid-state Batteries Based on Garnet Electrolytes

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The solid-solid interfacial contact is a critical issue during the studies of solid-state batteries (SSBs), which greatly affects the electrochemical performance of SSBs, such as the Coulombic efficiency, and cycle life. For flexible polymer/garnet electrolytes (PGEs), the interfacial issue mainly comes from the interactions between the inorganic fillers and the polymer matrix. The slow Li^+ transport through the polymer/garnet interface can lead to the low ionic conductivity of PGEs. While for garnet ceramic electrolytes (GCEs), the ceramic bulk with a relative density over 99% shows no obvious grain boundary, leading to the ionic conductivity over 10^{-3} S cm^{-1} at room temperature. Under this circumstance, the interfacial issue could be attributed to the poor interfacial contact between the GCEs and Li metal anodes. It can induce the large interfacial resistance as well as the lithium dendrite growth. In this presentation, I'll focus on the aforementioned interfacial issues, various targeted strategies will be introduced to construct the excellent interfacial structure, thus significantly improving the performance of SSBs [1-3].

Keywords: Garnet; Solid-state batteries; Interfacial engineering; Li dendrite suppression

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Graphene Based Hybrid Electrodes for Supercapacitors

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ABSTRACT

Supercapacitors are a promising energy storage system owing to their high power density and long cycling life [1]. One of the limitations, however, is their low energy density as compared to the batteries which hinders their wide applications [2]. This problem can be effectively solved by designing the hybrid electrodes: combining capacitor and battery materials to result in synergistically high electrochemical performance by incorporating two distinct energy storage mechanisms in a single device [3].

We report two hybrid electrodes designed by using graphene-based conductive matrix and compositing them with high capacity bimorph akaganeite and manganese dioxide nanoparticles [4,5] *via* a simple hydrothermal self-assembly method. The resultant nanocomposites have a high surface area and a large number of mesopores which facilitate channels for ion transport [4]. When used as the electrodes in symmetric and asymmetric supercapacitors in an aqueous electrolyte system, excellent energy-power profile, high specific capacitance and remarkable cyclic stability of up to 99.8% after 20,000 galvanostatic charge-discharge cycles have been obtained. This performance is attributed to a dominant capacitive charge storage mechanism by the synergistic combination of the components of the nanocomposites, well-structured hybrid electrodes, and chemically bonded components. This approach can be useful in designing high-performance electrodes for long life supercapacitors with both high energy and power densities.

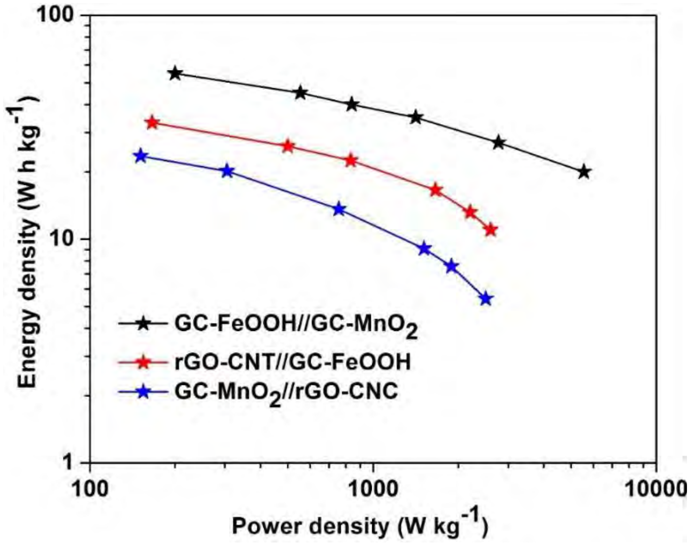

Figure 1. Energy-power profile of designed supercapacitor systems.

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Rational Material Design for Ultrafast Rechargeable Organic Lithium Ion Batteries

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It is very important to design the devices capable of fast charging and long life for commercial application. But fabrication of lithium ion batteries with high power and energy density is quite challenging. In recent years, a lot of work has been done to improve the rate performance and life of LIBs.[1] We believe that better understanding of the kinetics limitations for faster batteries can guide us to design materials for ultrafast long-life batteries.[2] To prove this, we started exploring redox active conjugated microporous polymers as an electrode for LIBs. In these systems interconnected microporous network can facilitate faster diffusion of ions. Large surface area can make the deep buried active sites accessible on or near to surface and conductivity can be improved by making composite with suitable conductive media. Combining all these effects together we were able to develop a lithium ion cell that can be charged as fast as 66C with significant capacity retention. Also, we found that cell can be charge and discharge for 3000 cycles without any capacity loss. Through carefully investigation we revealed that high surface area, porosity, and conductivity lead to energy storage process through surface or near surface pseudo capacitive energy storage mechanism which is usually found in supercapacitor and is faster than batteries. This study shows how we can transfer kinetically slow, diffusion controlled faradic reactions in batteries to faster pseudo capacitive reactions by rationally designing the materials.[3] We expect that this will pave the way for high power batteries with high energy density.

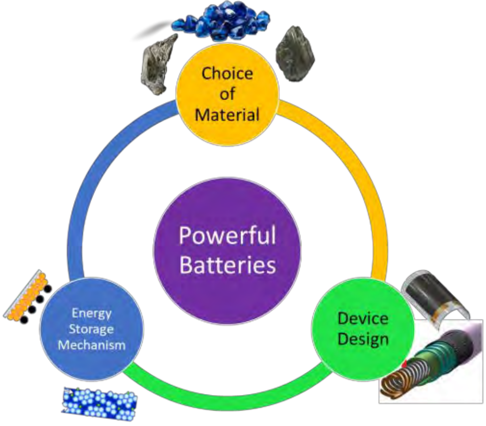

Figure 1: Important factors need to consider for high-power high-energy density batteries

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Probing Single-Particle Electrocatalytic Activity at Facet-Controlled Gold Nanocrystals

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Electrocatalytic reduction reactions (i.e., the hydrogen evolution reaction (HER) and oxygen reduction reaction) at individual, faceted Au nanocubes (NCs) and nano-octahedra (ODs) expressing predominantly {100} and {111} crystal planes on the surface, respectively, were studied by nanoscale voltammetric mapping. Cyclic voltammograms were collected at individual nanoparticles (NPs) with scanning electrochemical cell microscopy (SECCM) and correlated with particle morphology imaged by electron microscopy. Nanoscale measurements from a statistically informative set of individual NPs revealed that Au NCs have superior HER electrocatalytic activity compared to that of Au ODs, in good agreement with macroscale cyclic voltammetry measurements. Au NCs exhibited more particle-to-particle variation in catalytic activity compared to that with Au ODs. The approach of single-particle SECCM imaging coupled with macroscale CV on well-defined NPs provides a powerful toolset for the design and activity assessment of nanoscale electrocatalysts.

Voltammetric characterization of hesperidin with electroactivated pencil graphite electrode

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Flavonoids represent a large group of polyphenolic compounds which are widely distributed in plants and show beneficial effects on human health. Their biological activity can be connected with structural diversity and a wide range of their derivatives. Hesperidin is a phytochemical classified as bioflavonoid and can be primarily found in citrus fruits as well as in some other fruits and vegetables. Due to the suppression of pro-inflammatory cytokine production and its antioxidant defense mechanism, hesperidin shows different pharmacological activities such as cardio protective, antihypertensive, antidiabetic, anti-inflammatory, and antihyperlipidemic activity [1]. Graphite can be used as an electrode material since it has nonmetallic and metallic properties. The pencil graphite leads are composite materials which contain approximately 65% of graphite, approximately 30 % of clay, and around 5 % is a binder (wax, resins, or high polymer) [2]. The use of a disposable pencil graphite electrode (PGE) is proven to be a simple, cheap, and fast alternative with superior sensitivity and performance compared to more expensive electrodes [3].

In this study, PGE and electroactivated pencil graphite electrode (ePGE) were used for voltammetric characterization of hesperidin in model system with cyclic and differential pulse voltammetry. Both electrodes were characterized with electrochemical impedance spectroscopy (EIS) and scanning electrochemical microscopy (SECM) and the enhancement of electron transfer kinetics was observed after electroactivation. The effect of scan rate, pH, and hesperidin concentration on oxidation peak current were also studied. It was determined that oxidation peak current increases with the increase of scan rate and hesperidin concentration. The hesperidin oxidation was the most pronounced at pH = 5. The peak current and the hesperidin concentration showed linear dependence in the concentration range from 5×10^{-7} mol dm^{-3} to 1×10^{-5} mol dm^{-3}. Estimated limit of detection (LOD) was 5×10^{-7} mol dm^{-3}.

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Cathode Materials for Metal-Air Batteries based on Titanium Compounds

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TiO_xN_y powders were synthesized by sol-gel using titanium (IV) isopropoxide. Interconnected porosity was incorporated through phase separation of hydrophilic and hydrophobic blocks, and elimination of organic components with a thermal treatment. Partial substitution of oxygen by nitrogen was accomplished using thermal treatment in NH_3 atmosphere and incorporation of urea during the synthesis procedure. Powder characterization includes surface area (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD) and cyclic voltammetry (CV). The results show a high surface area around 200 m^2/g and a combination of titanium oxides, nitrides and oxinitrides.
These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Self-assembly of Mesoporous Nanostructured Catalysts for Enhancing the Electrochemical Energy Reactions

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Abstract

Nanostructured mesoporous materials are of interest for a variety of applications for developing renewable and clean energy sources. This work presents the synthesis of entirely new classes of nanostructured mesoporous transition metal oxides, hydroxides and phosphate nanocatalysts with improved electrocatalytic properties for hydrocarbon oxidation, water splitting, and fuel-cell reactions [1-5]. Mesoporous nanocatalysts of nickel, cobalt, tungsten and titanium oxides, hydroxides and phosphates with high surface areas, mesoporosity, and different nano-architectures are prepared via the surfactant template chemical deposition and hydrothermal approaches. The compositions, periodicities, surface areas, pore diameters, and architectures of the nanocatalysts can be varied in a controllable way through changes in the template compositions and deposition conditions. The electrochemical and catalytic activity of the resulting mesoporous nanocatalysts investigated and screened for electrochemical energy reactions of hydrocarbon (urea, methanol) oxidation and water splitting reactions of hydrogen, oxygen evolution and oxygen reduction reactions.

Keywords: *Mesoporous; Oxides; Phosphates; Energy Reactions.*

Acknowledgements

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Lithiophilic Polymer Interphase Anchored on Laser-punched 3D Holey Cu Matrix Enables Uniform Lithium Nucleation Leading to Super-stable Lithium Metal Anodes

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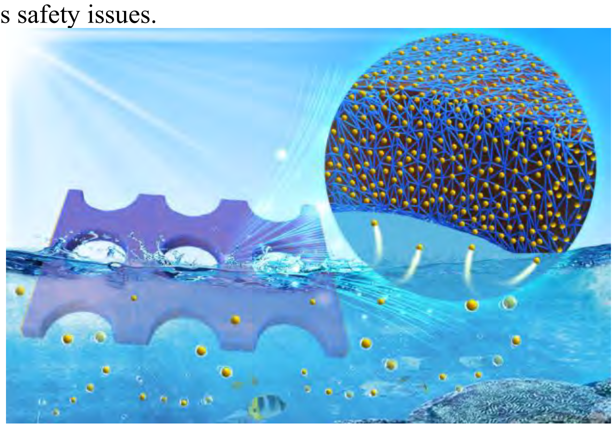
High energy density, long cycle lifespan, sufficient safety along with low manufacturing cost are among the ultimate goals for both the widely used lithium-ion batteries (LIBs) and other battery types. Owing to the high theoretical specific capacity (3860 mAh g^{-1}), lowest reduction potential (-3.04 V) and ultra-small theoretical density (0.534 g cm^{-3}), metallic lithium is regarded as the “Holy Grail” among various anode materials for the next-generation rechargeable batteries. Unfortunately, the inhomogeneous Li deposition and uncontrolled dendrite growth during repeated cycling lead to low Coulombic efficiency, poor performance, and serious safety issues.



Herein, a novel two-pronged strategy is proposed to effectively guide Li nucleation and suppress the unwanted Li dendrites growth, by a synergized approach of combining the laser-machined 3D holey Cu matrix (3D Cu) and lithiophilic polydopamine (PDA) surface coating layer. The PDA@3D Cu scaffold is shown to exhibit the wanted dendrite-free Li plating/stripping behavior. It delivers a remarkable Coulombic efficiency of 96.4% after 150 cycles (2.0 mA cm^{-2} at 1.0 mAh cm^{-2}), and achieves an excellent lifespan of over 1000 h operation tested in Li/Li symmetric cells, together with good stability for Li//$FePO_4$ full batteries. Our molecular dynamics (MD) simulations, density functional theory (DFT) calculations, and *in-situ* real-time monitoring using optical microscopy together have established the direct correlation between reversible Li electrodeposition and lithiophilic 3D holey structure scaffold. Significantly, the new findings suggest that a synergistic combination of 3D Cu with lithiophilic PDA coating layer represents an effective pathway to regulate metallic Li anodes towards practical applications.

Acknowledgements

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Electrochemical Behaviour and Anodic Dimerization of New Donor Acceptor Oligothiophenes for Organic Electronics Applications

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The term Organic Electronics is used to indicate the vast field of science regarding the use of organic materials (either "small" molecules, oligomers or polymers) in electronic devices. Thiophene derivatives are among the most studied and used organic semiconductor materials due their excellent charge transport properties and well-established synthetic procedures. These requisites are fulfilled by oligothiophene derivatives: in many cases they possess better characteristics (physical, optical, electronic and self-assembly properties, possibility to work in solution, ease of purification, low-cost synthetic procedures, and so on) over their polymeric counterparts. Electrochemical studies on a series of new conjugated oligothiophene derivatives are carried out. The molecular architectures (D-π-A and A-π-D-π-A, Figure 1) of these compounds present different donor cores (thiophene, bithiophene) with different numbers of 3-octylthiophene units (that act as π-bridge and solubilizing components). The acceptor end groups adopted were, in all the cases, ethyl cyanoacrylate units. The obtained results from electrochemical studies gave us the possibility to develop a new synthetic strategy including electrosynthesis (Figure 2) with an approach more environmentally friendly than classical synthetic procedures.

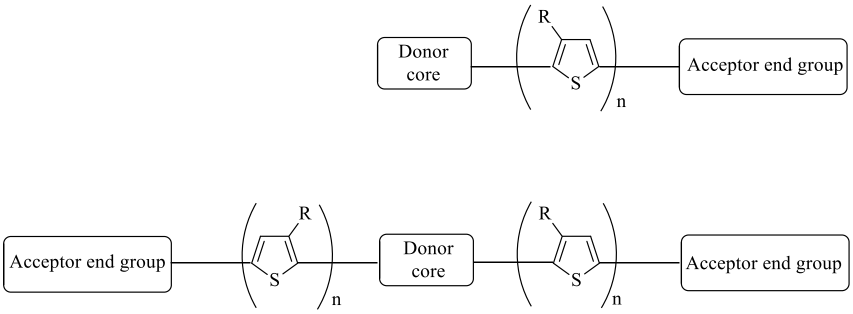
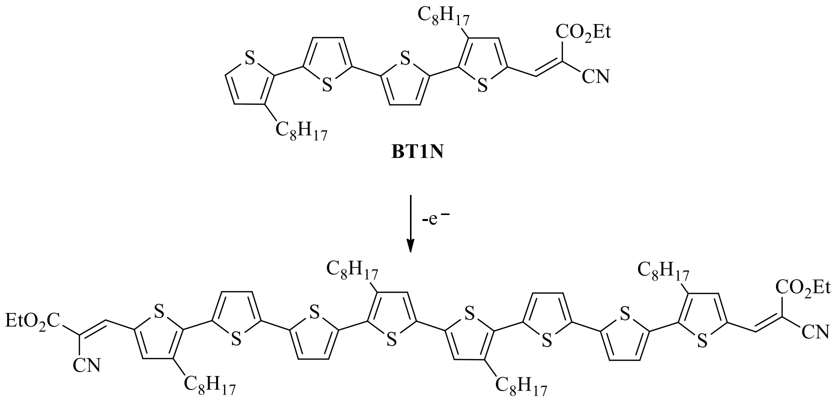


Figure 1. D–π-A and A–π-D–π-A molecular architectures adopted in this work.



BT1N

D8N

Figure 2. Anodic dimerization of a D-π-A oligothiophene (BT1N).

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Hydroxyapatite/Chitosan/Collagen Coatings By Galvanic Coupling

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For orthopedic prosthesis, titanium alloys, chromium alloys or stainless steel are suitable materials since mechanical properties are more similar to human bones. However, metal ions or nanoparticles release could produce Adverse Local Tissue Reactions (ALTRs) around periprosthetic tissues of the patients during post-surgery period [1], causing pain and rejection effects. In addition, corrosion phenomena could be occurred since after surgery, the local pH could be decreased around 5. Covering the metal substrate with biocoatings could be a solution in order to overcome these issues. In the last decades, many works were focused on composite coatings not only to improve the corrosion resistance but also to increase biocompatibility with human environment. In fact, in composite coatings the different components are able to act synergistically to give properties superior to those provided by component alone. Among the different composite coatings, those ones based on calcium phosphate compounds are the most interesting. In particular, hydroxyapatite is largely studied, since bones are constituted by hydroxyapatite crystals interspersed in the collagen fibers. Considering the bone structure, it is clear that a composite coating of hydroxyapatite and collagen could improve the performance of an orthopedic prosthesis. Another interesting material is chitosan, that is increasingly used in biocoating technologies thanks to its bioactive and biocompatible features.

In this work Hydroxyapatite/Chitosan/Collagen composite biocoating on AISI304 Stainless Steel was investigated. Biocoatings were realized through the deposition method of galvanic coupling. This process occurs without external power supply, because starting just from the coupling between two materials with different standard electrochemical potential [2-5]. In particular, the corrosion of the material with the low redox potential (sacrificial anode) produces the electrons necessary for the deposition. Electrons flow towards the cathode, where are used to produce hydroxyl ions thanks to electrogeneration of base reactions of nitrate ions and water molecules. The increasing of local pH at electrode/electrolyte interface leads to the deprotonation of amine groups of chitosan (pKa=6.4) while positively charged collagen fibrils start to self-assemble into fibers. Simultaneously, several equilibria reaction cause the precipitation of calcium phosphate (brushite/hydroxyapatite). The global process is the co-deposition of three components with the hydroxyapatite crystals that are incorporated in polymeric composite chitosan/collagen.

Physical-chemical characterizations of the samples were executed in order to evaluate morphology and chemical composition. In addition, potenziodynamic polarization and electrochemical impedance spectroscopy were carried out in a simulated body fluid to scrutinize the corrosion resistance. Furthermore, the metal ions release due to corrosion phenomena were quantified through Inductively Coupled Plasma Optical Emission Spectrometry. Also, cytotoxicity tests using MC3CT cells line was carried out in order to verify coatings' biocompatibility.

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Defect Chemistry of Electrocatalysts

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Abstract

Surface engineering on the electrocatalyts is one of the most popular strategies to tune the electrocatalytic activities. Here, we will present our recent progress on the Co-based electrocatalyst for oxygen evolution reaction (OER), which is the key process for metal-air batteries, and water splitting. Currently, the typical electrocatalyst for OER is RuO2 and IrO2-based precious metal compounds. However, these noble metal-based electrocatalysts are of high cost and poor stability. Therefore, various strategies have been developed to enhance the electrocatalyst performance through the surface control. Recently, we have developed the plasma technology to tune the electrocatalytic performance of carbon-based metal-free electrocatalyst, Co-based compound and 2D layered nanomaterials for OER. In this talk, we will focus on the recent development of plasma treated electrocatalysts in the aspects of defect chemistry.

IrO_2/Ir/Ti and IrO_2/Ir(Ni)/Ti Oxygen Evolution Anodes prepared by Galvanic Deposition and Galvanic Replacement

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IrO_2-modified Ti electrodes have been prepared by either a simple galvanic deposition process or a Ni-mediated galvanic replacement method. In the former case a freshly etched Ti substrate has been treated with an Ir(IV) solution, resulting in the spontaneous deposition of metallic Ir on the surface of the Ti substrate with the simultaneous oxidation of nearby freshly etched Ti sites [1]. In the latter case, a smooth Ni film has been electrodeposited on the Ti substrate from a Watts bath and its surface layers spontaneously exchanged with metallic Ir upon treatment with an Ir(IV) solution [2-3]. Anodization of the resulting Ir/Ti and Ir(Ni)/Ti electrodes by means of continuous potential cycling in acid solutions resulted in the formation of IrO_2 porous surface layers (or IrO_x, depending on the positive potential limit), showing typical Ir oxide surface electrochemistry (*Figure 1*). SEM pictures revealed that the thus prepared IrO_2/Ir/Ti electrode is made of sparse IrO_2/Ir micrometer-sized islands and nanoparticles, while the IrO_2/Ir(Ni)/Ti electrode consisted of a continuous film with a nodular morphology (as confirmed by AFM). The composition of the coatings was estimated by EDS and XPS spectroscopy while Ir mass loading was determined by ICP-MS following etching in acid. These electrodes have been tested as oxygen evolution reaction (OER) anodes by slow potential sweep voltammetry *(Figure 2)*. IrO_2/Ir/Ti electrodes exhibited mass specific activities for OER (ca 200 mA mg_{Ir}^{-1} at η=300 mV) better or comparable to traditional Ir DSAs [4] or state-of-the-art thin thermal films [5], whereas the IrO_2/Ir(Ni)/Ti electrodes were proven comparable or better than both state-of-the art thin thermal films [6] and nanoparticle $IrNiO_x$ catalysts [7] (ca 2 A mg_{Ir}^{-1} at η=300 mV). The recently established enhancement of IrO_2 OER activity by Ni, combined with the widespread use of Ti as a stable electrode substrate, make IrO_2/Ir(Ni)/Ti attractive DSA electrodes.

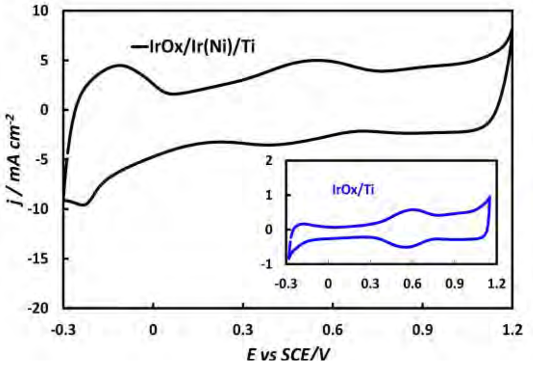

***Figure 1** Cyclic voltamograms (at 100mVs^{-1}) of IrOx/Ir(Ni)/Ti and IrOx/Ti (Inset) electrodes in a 0.1 M deaerated $HClO_4$ solution*

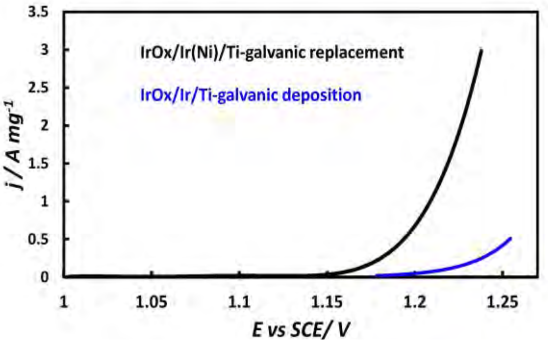

***Figure 2** Linear sweep voltamograms (at 5mVs^{-1}) of IrOx/Ir(Ni)/Ti and IrOx/Ti (Inset) electrodes in a 0.1 M deaerated $HClO_4$ solution*

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In Vitro Redox Activity of Haemozoin and β-Haemozoin Interacting with Artemether, Lumefantrine and Quinine.

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Abstract. In the malaria disease, the released haem group into erythrocytes is oxidized to haematin and inert dimeric haemozoin bio-crystals form, which provides the parasite a unique way to avoid the toxicity associated with the haem group. Due that, antimalarial drugs to inhibit dimer formation; however, recent electrochemical studies indicate that an inert dimer also promotes a toxic oxidizing environment. This work explores drug reactivity with monomers and dimers and their contribution to maintain redox balance. Materials and methods. Through cyclic voltammetry three medicines mixed with haemozoin or β-haemozoin were tested. Results and discussion. The data indicated again that the drugs "*per se*" (Figure 1) and in combination (Figures 2 & 3), modify the natural redox state of haemozoin and β-haemozoin. The natural oxidation potential of the drugs alone was evident. It was found that the oxidation potential decreased through quinine, lumefantrine and artemether with the same tendency in the haemozoin presence but with less current density. Finally, the oxidation response between the monomer haemozoin and antimalarial drugs is carried out at more negative potentials.

The results indicate that antimalarials *per se* can contribute to oxidation processes and that in combination with monomeric or dimeric haemozoin can increase or decrease the oxidizing power of the haemozoin forms. The various oxidizing environments suggest that the cell membranes can also be damaged by the unique presence of the antimalarial. To maintain the intracellular redox balance is very important, so indicate treatments that could potentially alter it, (artemether) or (benflumetol,) should consider that maybe there will be an imbalance.

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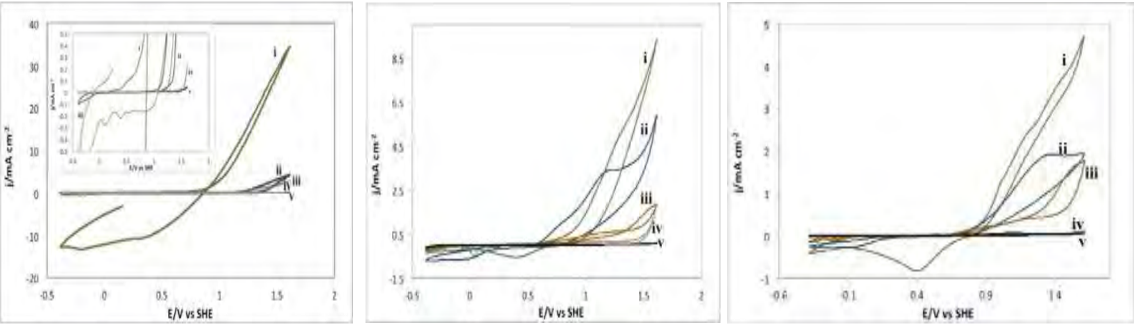

Figure 1, on left. CV on CPE-AQ (green curve, i), CPE-CQ (blue curve, ii), CPE-QN (orange curve, iii), CPE-ART (gray curve, iv) and CPE-LF (black curve, v) anodic direction. Figure 2, in the middle. CV of CPE-AQ-Hz (green curve, i), CPE-CQ-Hz (blue curve, ii), CPE-QN-Hz (orange curve, iii), CPE-ART-Hz (gray curve, iv) and CPE-LF-Hz (black curve, v). Figure 3, at right. CV on CPE-graphite-Hz-LF (a); CPE-graphite-Hz-ART(b); CPE-graphite-β-Hz-LF (c) and CPE-graphite-β-Hz-ART (d).

Removal of Pesticides by Coupled Electrochemical and Photochemical Oxidation

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The pesticides Thiamethoxam (THI), Acetamiprid (ACT), Imidacloprid (IMI) and Thiacloprid (TCP) are four examples of common chemicals used in the control of plagues in agriculture. The manufacturing, formulation, storing, manipulation and use of pesticides generate effluents difficult to treat due to the high toxicity of those compounds. This work tests the use of photochemical and electrochemical oxidation as an effective method to eliminate pesticides from aqueous effluents. Both, the photochemical and the electrochemical oxidation were able to oxidize the pesticides molecules, but the efficiency largely depended on the chemical nature of the compounds. THI was easily degraded with UV-C light photochemical oxidation, whereas TCP was removed by electrochemical oxidation. ACT was the compound that showed the highest resistance to be degraded by both, photochemical and electrochemical oxidation. The combination of the photochemical and the electrochemical oxidation in a dual reactor (a reactor with two separate chambers for the photochemical and electrochemical reactions) enhanced the degradation of the THI, IMI and TCP reaching a complete removal in 1 h. ACT was only removed by 50% in 2 h. the removal of ACT was enhanced up to 70% in 2 h by electro-Fenton oxidation, using ferrous iron in the effluent treated in the electro-photochemical reactor.

Combination of Electrochemical and Photochemical Methods for TOC/COD Removal in Industrial Effluents

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Activated carbon is a common adsorbent material for the retention of organic and inorganic contaminants. Various industrial sectors use activated carbon in purification of liquid and gaseous streams and in the retention of valuable materials. These industrial sectors include Au mining, water purification, pharmaceutical and chemical industry, etc. The reactivation and reuse of the spent activated carbon is a more sustainable practice than "one-use" and dumping. However, the classical thermal regeneration of activated carbon shows a large impact due to the emission of CO_2 and the partial loss of carbon and activity. The electrochemical regeneration of saturated activated carbon has been proposed as an efficient and sustainable alternative to the classical reactivation methods. The electrochemical treatment consumes less energy and produces less CO_2 than the traditional thermal activation. The electrochemical regeneration of activated carbon is based on the application of a DC electric current directly to the carbon specimen using a solution of sulfuric acid as electrolyte. The electric current desorbs and mobilizes the contaminants retained in the activated carbon. The contaminants include organic compounds and inorganic ions. At the end of the regeneration process, the contaminants released from the carbon remains in the electrode solutions (anolyte and catholyte). Such end-waste effluents require treatment before their final disposal. This work has analyzed the chemical composition of the end-waste effluents and have proposed and tested various technologies for the separation/degradation of organic and inorganic contaminants. The chemical neutralization and precipitation of the contaminants is a practical method to remove all the toxic metals in the effluent that it can be discharged directly in the sewage system. The precipitation with NaOH, $NaCO_3$, $CaCO_3$ and CaO showed similar metal removal results, but the precipitation with $CaCO_3$ showed the additional benefit of TOC and nitrogen removal. Despite the good results of the neutralization/precipitation method, this treatment did not allow for the recycling of the effluent to the activated carbon regeneration process. Various advanced oxidation processes (electrochemical, photochemical and chemical oxidation) have been tested to identify an alternative method that allowed for the recycling of the effluent to the carbon regeneration system. A combination of electrochemical and photochemical oxidation with persulfate was identified as a practical treatment to remove the TOC and COD from the effluent. The electro-photochemical treatment was able to remove all the organic contaminants in the effluent, expressed as COD, in 8 h with 16 W UV-C lamp and an electric consumption of 5.7 Wh/L. The treated effluent can be recycled back to the electrochemical regeneration system.

Bioelectrochemistry of neuronal protein tau

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Tau is a neuronal protein and one of the biomarkers of neurodegenerative diseases, such as Alzheimer's disease. Tau protein undergoes post-translational modifications, aggregation, and is a viable drug target. In addition, this protein is a vital biomarker in biological fluids towards early detection of neurodegenerative diseases. We reported on using electrochemical impedance spectroscopy and cyclic voltammetry for detection of protein-protein interactions (1), protein-ligand interactions (2), enzymatic catalysis and enzyme inhibition (3) while focusing on tau protein and its biochemistry. For example, tau-tau, tau-ferritin, tau-transferring protein interactions were monitored, and protein kinase-catalyzed phosphorylation of tau protein was detected. The phosphorylation inhibitors, such as antibodies, were screened for their efficacies. New research directions in neuroelectrochemistry of tau protein alongside other neuronal biomarkers, such as Amyloid beta and alpha synuclein, will also be described.

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Exclusive solution discharge in Li-O_2 batteries as revealed by *operando* X-ray scattering

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Lithium-air (Li-O_2) batteries promise a drastic increase in energy densities and a reduced ecological footprint compared to intercalation-type Lithium-ion batteries. Considering mass and volume of non-active materials, real performance improvements are only achieved if lithium peroxide (Li_2O_2) is packed as dense as possible in the nanoporous carbon cathode host. [Freunberger, S. A. , *Nature Energy* **2**, 17091 (2017)]. To understand how structural features of the formed Li_2O_2, dynamic phenomena during product growth and the underlying reaction mechanisms determine the discharge capacity, quantitative real-time in situ metrologies with structural information at the atomic to micron level are required.

Here we present *operando* small and wide angle X-ray scattering (SAXS/WAXS) as a novel method to study the morphological evolution of Li_2O_2 during charging and discharging a custom-built in situ Li-O_2 cell [*ChemRxiv* 2019, DOI 10.26434/chemrxiv.11447775.v1]. For data analysis a recently developed method was adapted [Prehal, C. *et al.*, *Nature Energy* **2**, 16215 (2017)] and synergistically combined with modelling of Li_2O_2 nucleation and growth in a realistic 3D carbon pore model. This allows visualizing the nanoscale product formation in real-time and distinguishing between Li_2O_2 formed via disproportionation (solution mechanism) or a second, consecutive electron reduction (surface mechanism). We show that Li_2O_2 is formed exclusively via solution mediated disproportionation of LiO_2 across the whole range of organic electrolytes and carbon electrodes. Deciding for particle morphology is the concentration distribution of associated LiO_2 in solution, governing nucleation and growth rates of Li_2O_2 formation. Discharge capacity and Li_2O_2 pore filling hence equally depends on electrolyte solvation energies, true areal current densities and species mobilities in solution. Given that species mobilities are high and current densities low, this allows for high discharge capacities even in low donor number electrolytes, previously thought to be prototypical for Li_2O_2 surface growth with poor discharge capacities. Next to rotating ring disc measurements, electron microscopy and numerical modelling, *operando* SAXS/WAXS was the essential tool for these insights. On a wider perspective *operando* SAXS/WAXS proofs as a powerful *in situ* metrology to study electrodeposition in all conversion-type batteries and more generally structural changes in complex electrochemical energy storage systems at length scales ranging from atomic to sub-micron resolution.

Exploiting glucose meters for early detection of prostate cancer

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Cancer is a major global public health problem with enormous human and economic costs [1]. Liquid biopsy has emerged as a potential supplement of traditional biopsy for early cancer diagnosis. Specifically, appropriate bodily fluids are analysed to monitor the level of tumour biomarkers present in the medium. There is, therefore, a clear need to develop non-invasive, easy-to-use and inexpensive methods for the detection of biomarkers that allow improving diagnosis and minimizing the mortality of cancer, while reducing healthcare expenditure of cancer care. In this context, electrochemical platforms have demonstrated great potential due to their high sensitivity, low cost, fast response as well as compatibility with point-of-care (POC) testing, what contributes to decentralize the analyses and favours the implementation of screening studies. Among them, personal glucose meter (PGM) employed daily in the measurement of blood glucose is the most used analytical method worldwide. Taking advantage of this mature technology, PGM has been recently applied to quantitate a wide range of non-glucose analytes by establishing a relationship between their recognition and glucose generation [2]. This strategy is of particular interest for monitoring tumour biomarkers since PGMs are already approved by international agencies for application to clinical practice, thus paving the way for the launch of the new device to the market.

Thus motivated, we describe the development of a hybridization assay for the detection of prostate cancer antigen-3 o PCA3, a urinary RNA biomarker for prostate cancer diagnosis [3]. Specifically, a sandwich-type genoassay has been implemented onto magnetic microparticles functionalized with streptavidin in combination with a personal glucose meter and alkaline phosphatase (ALP) as a glucose-generating enzyme for signal transduction. Moreover, with the goal of detecting clinically relevant PCA3 levels, an isothermal DNA amplification strategy such as Rolling Circle Amplification (RCA) has been designed [4]. In this strategy, a circular DNA called padlock acts as a template for the phi29 polymerase, which is capable of generating thousands of padlock copies, resulting in multiple binding sites for a fluorescein-tagged reporting probe. Numerous antifluorescein-ALP conjugates are then incorporated per target analyte, for enzymatic conversion of glucose-1-phosphate into glucose, whose concentration is subsequently determined with a glucometer. This isothermal and portable approach allows the reliable detection of PCA3 at picomolar levels.

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Acknowledgements

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New insights into the mechanism of coreactant electrogenerated chemiluminescence facilitating enhanced bioanalytical performance

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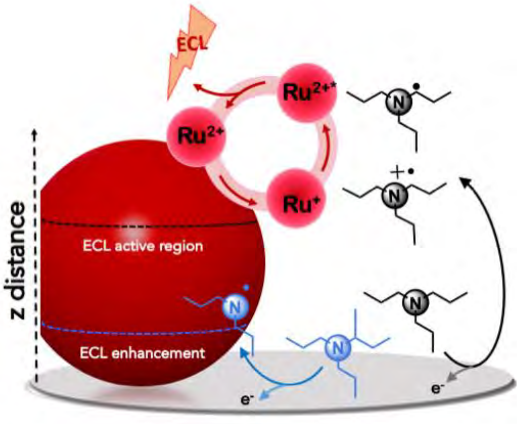
Electrochemiluminescence (ECL) is a leading technique in bioanalysis.[1] Since the excited species are produced with an electrochemical stimulus rather than with a light excitation source, ECL displays improved signal-to-noise ratio compared to photoluminescence, with minimized effects due to light scattering and luminescence background. The most challenging breakthrough in the development of analytical electrochemiluminescence (ECL) applications was reported from Bard and co workers that presented for the first time the generation of ECL with a coreactant.[1] This finding opened the application of ECL to large literature and transformed ECL from an academic curiosity to a real application and industrial success. In this context, the only real used materials for the ECL analytical and commercial application are tripropylamine (TPrA) as sacrificial "oxidative-reductant" coreactant and Ruthenium(II)-tris(2,2'-bipyridine) ($[Ru(bpy)_3]^{2+}$) as emitting species. In this case the mechanism for the ECL generation was proposed by Bard and still nowadays the only one accepted.[2],[3]

Here we show an additional, and very efficient, mechanism pathway for the generation of ECL by using TPrA as coreactant. Thanks to the combination between ECL and microscopy we experimentally prove the alternative mechanism with the standard $[Ru(bpy)_3]^{2+}$/TPrA system.[3],[4] These mechanistic findings allow us to propose alternative amines as coreactant enhancing the ECL signal of more than one order of magnitude.

The reported results, besides contributing to a better understanding of the mechanisms operating in the chemiluminescence generation, also pave the way for the development of very highly efficient ECL coreactants for ultrasensitive bioanalysis.[5]



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Photoelectrochemical CO_2 Reduction in Aqueous and Room-Temperature Ionic Liquids-Based Media by Scanning Electrochemical Microscopy

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The photoelectrochemical (PEC) carbon dioxide (CO_2) reduction reaction (CO_2RR) can convert CO_2 to various products such as carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), methanol (CH_3OH), which can contribute to remit environmental and energy issues caused by increasing CO_2 concentration. The Scanning Electrochemical Microscopy (SECM)[1] employs an ultramicroelectrode (UME) as the tip to apply a suitable potential and collect the corresponding electrochemical signal response as a current, which allows to explore the electrocatalytic properties of different materials. The UME tip can be replaced by an optical fiber (OF), which is connected to a Xenon light source and provides UV-visible or visible light. This illumination can be locally driven on the candidate catalysts for PEC-CO_2RR activity evaluation by scanning photoelectrochemical microscopy (SPECM). Possessing many physicochemical properties, room-temperature ionic liquids (RTILs) can dissolve more CO_2 and inhibit competitive side reactions (ex: H_2 evolution) during CO_2RR. Furthermore, it is reported that the cation of imidazolium based RTILs ($C_n$mim$^+$) has a co-catalyst role for electrochemical CO_2RR on Ag electrode.[2]

In our work, we apply SPECM to locally illuminate p-type semiconductor materials such as $CuCo_2O_4$ immersed in different electrolytes solutions for evaluating the performance of PEC-CO_2RR. The PEC reduction currents obtained by SPECM in aqueous solution ($KHCO_3$), in binary mixture solution (25% [C_2mim][BF_4]/H_2O and 25% [C_4mim][BF_4]/H_2O) and in pure RTILs are compared in this work. We get a relevant increase in photocurrent in 25% [C_2mim][BF_4]/ H_2O mixture in comparison with all other media tested either under UV-Visible or Visible illumination, pointing out the co-catalyst role of imidazolium cation for the photoelectrochemical reduction of CO_2. In contrast, we find a decrease in photocurrent in 25% [C_4mim][BF_4]/H_2O mixture, probably due to the strong interaction of [C_4mim]$^+$ and CO_2. Meanwhile, as reported by Zigah et al,[3] we fabricated a dual tip which combined optical fiber and Pt UME (OF-UME) acting simultaneously as a light source and a sensor for detecting the PEC-CO_2RR products in SPECM.

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Chemically Modified Electrodes with Clickable Thiosemicarbazones for Metal Ions Sensing

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Originally designed as a tool in organic synthesis, the concept of "*click chemistry*" introduced by Sharpless and co. in 2001 [1] emerged very rapid as one of the most employed routes for designing the architecture and functions of different types of surfaces with important applications (e.g. nanomaterials) [2]. Moreover, due to the mild conditions, this method can be applied even in aqueous solvents in the presence of a catalyst and of many functional groups without protection. The process is fast, selective and resistant to side reactions. However, this approach has rarely been applied to modify electrodes with chelating groups for heavy metal ions sensing.

We report here, the synthesis of novel thiosemicarbazone ligands bearing azido groups, which were further immobilized on a phenylethynyl-functionalized glassy carbon surface, through a Cu(I)-catalyzed azide-alkyne cycloaddition reaction. In this manner, new modified electrodes were obtained, and their ability to coordinate metal ions, due to the intrinsic properties of the immobilized ligands, was studied.

Acknowledgements
The authors gratefully acknowledge for the financial support of the Romanian National Authority for Scientific Research, UEFISCDI, under grant PN-III-P1-1.1-TE-2016-0860, contract no. 114/2018.

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High-capacity and ultra-long-cyclability lithium–sulfur battery with a dual-porosity cathode matrix derived from brewing wastes

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The large development of renewable energy sources requires the parallel development of sustainable energy storage systems because of its non-continuous production. In this reality, the lithium–sulfur battery emerges as one of the most promising technologies to face this problem. Moreover, the use of biomass to produce cathodes for these batteries addresses not only the aforementioned problem, but also it reduces the carbon footprint and gives added value to something normally considered waste. In this work, we report the production, by simple and non-activating pyrolysis, of a carbon material using the abundant 'after-boiling waste' derived from beer brewing.[1]

In a typical fabrication, the after-boiling waste that come directly from the factory was dried overnight, then heated from to 900 °C for 60 min for carbonisation under a nitrogen atmosphere. No further activation or washing was needed. The material was named ABW-C.

Regarding the structural characterization, a carbon percentage of 88% was found by TG analysis on the ABW-C material in oxygen atmosphere. This is a value that confirms a material with a high carbon content, a strictly necessary condition for suitable carbon materials from biomass or industrial waste. The XRD pattern of the ABW-C shows the expected two broad peaks of low intensity, with the peaks centred at 25 and 44° coming from to the crystallographic planes of graphite (002) and (100), respectively. Pore size distribution calculated by DFT method revealed dual micro- and mesoporous structure of the ABW-C. From BET isotherm a total pore volume of 0.277 $cm^3\ g^{-1}$ with a micropore volume of 0.141 $cm^3\ g^{-1}$, can be calculated (approx. 50% microporosity).

After adding a high sulfur loading (70%) to this biowaste-derived carbon by the 'melt diffusion' method, the sulfur–carbon composite (ABW-C@S) was used as a cathode in Li–S batteries. The cathode exhibited excellent performance, reaching high capacity values and ultra-long cyclability at high current: 847 mAh g^{-1} (at 1C, Fig. 1), 586 mAh g^{-1} (at 2C) and even 498 mAh g^{-1} (at 5C) after 400 cycles, drastically reducing the loss of capacity per cycle to values close to 0.01% per cycle.

In conclusion, carbon derived from brewing waste, without any activation process, has demonstrated suitable textural properties for the preparation of high-sulfur-content composites to use as effective cathodes in Li–S cells. Its high surface area, combined with its interconnected micro- and mesoporous system, raises its performance, in both capacity values and cyclability, even at high current densities. Therefore, this work demonstrates the possibility of revaluing the brewing waste by transforming it into a porous carbon, using a simple process without activation stages, with promising performance in a sustainable cathode for ultra-high-cyclability Li–S batteries. In short, this work demonstrates the possibility of obtaining low-cost, highly sustainable cathodic materials for the design of advanced energy storage systems.

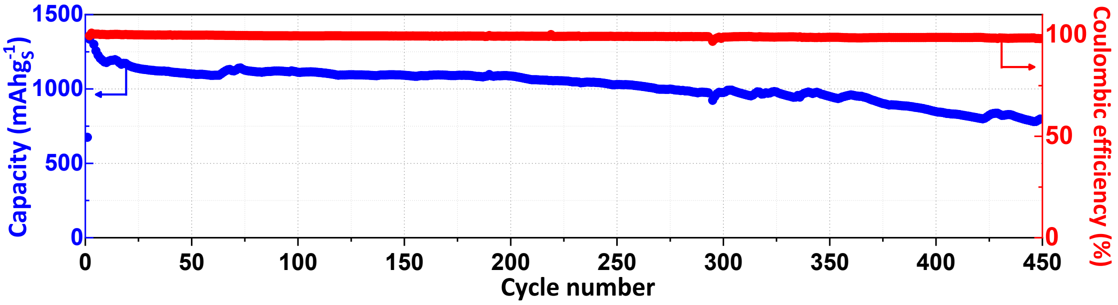

Figure 1. Long-term cycling performance of Li/LiTFSI-LiNO$_3$-DOL:DME/ABW-C@S at 1C (1675 mA g^{-1}).

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Hybrid Capacitor with Anthraquinone-Grafted Carbon as Battery-Type Electrode Operating in Low pH Aqueous Salt Solution

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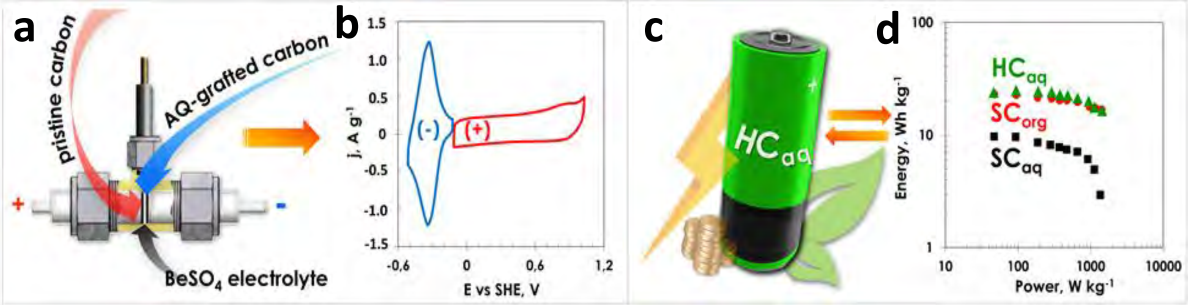
Hybrid capacitors combine one electrical double-layer electrode - usually a high surface area carbonaceous material, together with a faradaic battery-type component [1]. Recent examples of high conductivity battery-like electrodes are realized by operating carbon electrodes in a redox-active electrolyte [2] or by modifying carbon with electroactive molecules [3]. Grafted carbons, e.g., with anthraquinone (AQ) moieties, are recognized to display highly reversible redox activity in acidic electrolytes such as sulfuric acid, unlike in basic electrolytes where quinone-dianions are formed causing AQ detachment from the surface [3]. However, in H_2SO_4 electrolyte, expensive gold current collectors are required to avoid corrosion issues, and the operational voltage of carbon-based capacitors is restricted (~ 1V).

In the present study, anthraquinone (AQ) moieties (0.1eq. vs. carbon) have been grafted using the corresponding diazonium salts on the surface of the SC2A carbon black (Cabot, S_{DFT} =1502 m^2 g^{-1}, total pore volume = 1.05 $cm^3 \cdot g^{-1}$). The AQ mass loading in SC2A@AQ was ~16 wt% as determined by CV and TG analysis. The DFT specific surface area of SC2A@AQ was reduced to 191 m^2 g^{-1}, and the total pore volume dropped to 0.46 $cm^3 \cdot g^{-1}$. Despite the large difference in S_{DFT} values of the materials, the EDL capacitance values of SC2A and SC2A@AQ electrodes in 1 mol L^{-1} $BeSO_4$ (pH = 2.1) were comparable, owing to the improved wettability of the latter material. The performance of a (-)SC2A@AQ//SC2A(+) hybrid capacitor (HC_{aq}) in 1 mol L^{-1} $BeSO_4$ was characterized by a quasi-linear GC/GD profile and twice higher capacitance compared to the symmetric (-)SC2A//SC2A(+) cell. The capacitance retention of the HC_{aq} reached 87 % after 10,000 galvanostatic cycles up to 1.6 V. Owing to the AQ grafting, the negative SC2A@AQ electrode of the HC_{aq} demonstrated a very low potential decay (so-called self-discharge) of 0.11 V after 4-hour voltage hold at 1.5 V, as opposed to 0.92 V for the SC2A negative electrode in the SC_{aq}. Overall, the HC_{aq} delivered energy and power performance comparable with a symmetric SC2A/SC2A capacitor operating up to 2.7 V in usual organic electrolyte (SC_{org}), whilst succeeded by being an economically viable energy storage device.



Scheme 1: (a) hybrid cell with reference electrode (to study the behavior of individual electrodes) made of as received SC2A carbon black as positive EDL electrode and its modified SC2A@AQ counterpart employed as battery-type negative electrode operating in 1 mol L^{-1} $BeSO_4$ aqueous electrolyte; (b) cyclic voltammograms of the electrodes at cell voltage of 1.6 V; (c) illustration of the (-)SC2A@AQ//SC2A(+) hybrid capacitor (HC_{aq}) which ensures a low production cost, high power and energy; (d) Ragone plot of HC_{aq} and (-)SC2A//SC2A(+) symmetric (SC_{aq}) cells in $BeSO_4$ (range of 1.5-0.75 V) at constant power; it shows that HC_{aq} advantageously competes with the (-)SC2A//SC2A(+) cell in $TEABF_4$/ACN organic electrolyte (SC_{org}; in the range 2.7-1.35 V).

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Temperature Dependent Non-linear Electrochemical Impedance Spectroscopy Analysis to Elucidate the Solid Electrolyte Interface on Li Metal in Li\SOCl₂ Batteries

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The Solid Electrolyte Interface (SEI) plays a very important rule in the stability, safety and voltage behavior of Li based batteries. Lithium Thionyl Chloride (Li\$SOCl_2$) primary batteries are among the most used Li metal-based batteries due to high energy densities. The stability of the Li metal used as anode is governed by the SEI formed from the reaction of Li with the electrolyte $SOCl_2$ [1]. In the voltage performance of the battery, the SEI is shown to have drastic effect on the voltage behavior of the battery during operation [2].

The non-linear data obtained during the performance of Electrochemical Impedance Spectroscopy (EIS) measurements of Li\$SOCl_2$ can be used to study the SEI formed on the Li metal anode. The non-linear data is obtained as higher order harmonics which have certain amplitudes at the multiple frequencies of the excited signal as shown in Figure 1(a). In our previous work, we have shown that the presence of thicker and denser SEI causes non-linearities in the voltage response in the form of second harmonic signals in the non-linear harmonic spectrum shown in Figure 1(b) [3].

In this work, we will show the results obtained from the further investigation of the SEI on the Li anode by non-linear harmonic analysis coupled with temperature and State of Charge variations. The obtained harmonics provide information related to the formation and degradation kinetics and composition of the SEI. Further, the relation of varying electrode/electrolyte composition to the parameters of the SEI will be shown. The results will demonstrate how non-linear harmonics, which are usually avoided in EIS measurements, can be utilized to investigate the SEI in Li based batteries.

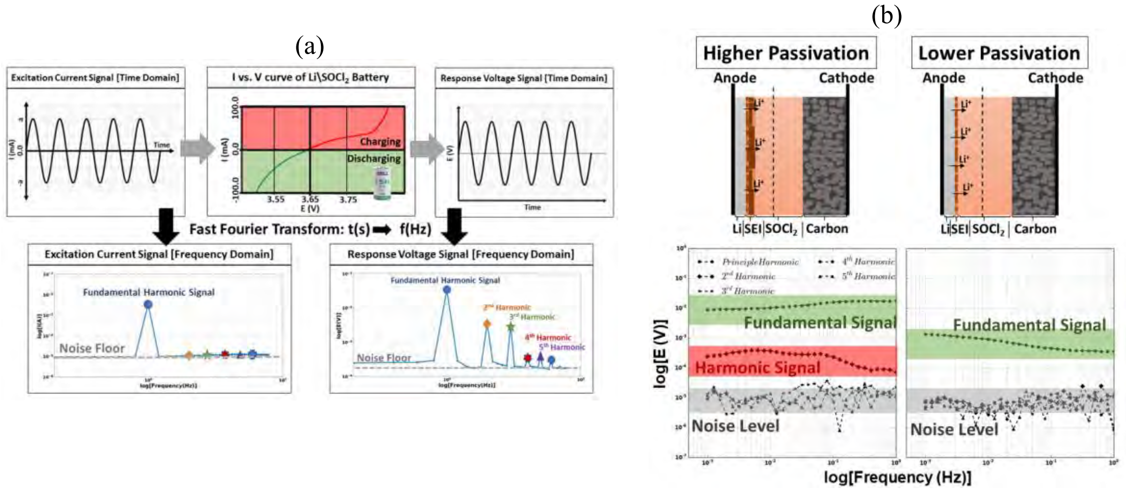

Figure 1. (a) Non-linear Harmonic Analysis for Li/$SOCl_2$ battery, (b) Non-linear harmonic spectra for cells with different Solid Electrolyte Interphase structure

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Liquid based synthesis of argyrodite structure solid electrolytes for all-solid-state batteries

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High energy density with safety is important point to develop the large sized batteries for electric vehicle. Safety issues of current lithium ion battery system mainly comes from the oxide cathode and flammable organic electrolyte. All solid state batteries with non-flammable inorganic solid electrolytes have received great attention from electric vehicle companies due to its potential for securing higher energy density and safe characteristics over current lithium ion battery system. A high lithium ion conducting solid electrolytes is core technology to the development of all solid state batteries. Solid electrolytes were mainly synthesized by solid state method with high energy ball milling and het treatment process. A high energy mechanical milling system is not sufficient for large scale synthesis process. Recently, new synthesis method with liquid based system was proposed to avoid milling process. Moreover, new materials might be synthesized via liquid based synthesis method which cannot be successfully obtained by solid state synthesis.

In this study, liquid based synthesis process was examined by controlling kinds of solvents, purity, reaction order, ratio of precursors and vacuum drying process. An argyrodite structure solid electrolytes, Li_6PS_5X (X=Cl, Br) were successfully synthesized by liquid based synthesis method. Crystallinity and ion conductivity was evaluated by X-ray diffraction method and AC impedance technique. All solid state batteries were fabricated by powder pressed type half-cell and electrochemical tests were investigated and the detailed results will be discussed in this presentation.

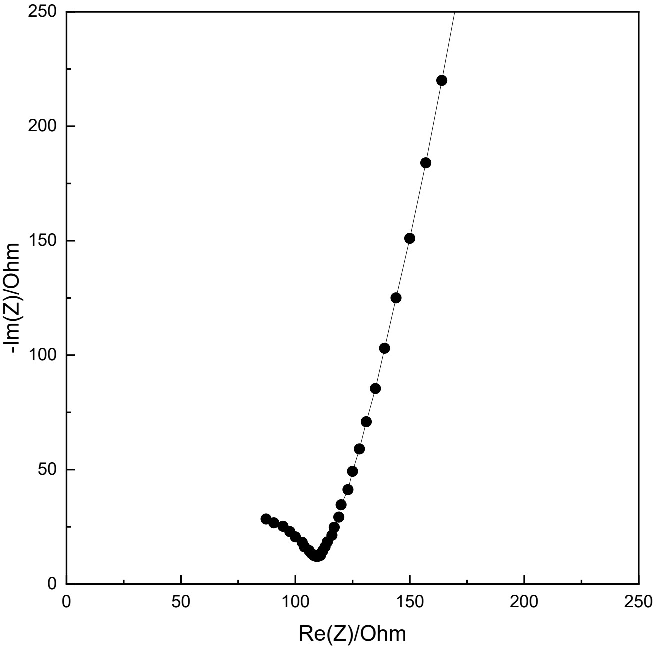

Fig 1. Nyquist plots of Li6PS5Br electrolyte obtained by liquid based synthesis method

Soft Obtaining of the Composite LiMn$_{1.6}$Ni$_{0.4}$O$_4$-LiFePO$_4$/C by Microwave Heating

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Simple preparation process by microwave heating to obtain composite materials LiFePO$_4$/C olivine (2% w/w) deposited as a coating on LMNO spinel (98% w/w) was studied in order to avoid the spinel phase dissolution in the liquid electrolyte. Microwave radiation allows local melting of the carbon precursor in the LiFePO$_4$/C resulting in a compact protective layer without further phase transition. The composite formation and the phase transitions during microwave heating were characterized by synchrotron XRD, SEM and TEM. The electrochemical performance of composite materials was characterized by charge/discharge cycling, rate-capability and electrochemical impedance spectroscopy (EIS). The degradation process after cycling was also characterized by synchrotron XRD. With a heating of 10W the composite LMNO-2LFP/C was obtained with superior crystallographic order without impurities precipitation, see Fig. 1a. This composite retains the 97% of initial capacity after 100 cycles and higher discharge capacity was achieved (see Fig. 1c). After 100 cycles, the composite material LMNO-2LFP/C-10W retains the lattice parameters of the spinel phase, while olivine phase is partially delithiated and additional peaks at 2θ of 9.35° and 14.85° significantly smaller than those of LMNO appear (see Fig. 1b). At heating power of 100W changes in the lattice parameters of spinel phase take place and impurities precipitate decreasing discharge capacity, possibly due to degradation of the spinel structure by overheating.

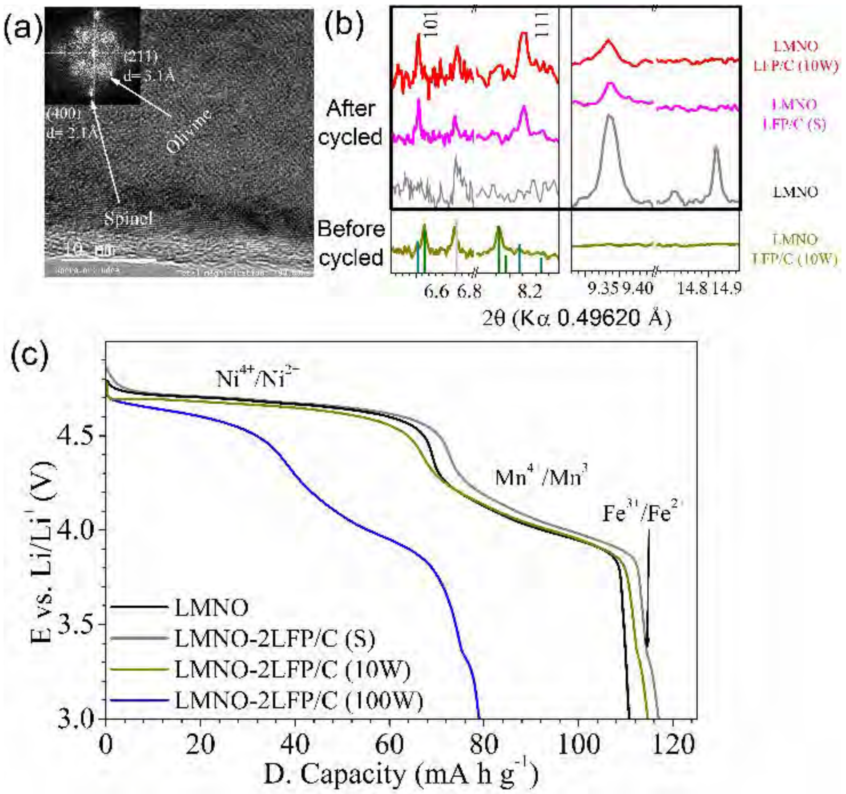

Fig. 1 (a) LMNO-2LFP/C (10W) TEM. (b) Synchrotron XRD of LMNO-2LFP (10W) before cycled and LMNO, LMNO-2LFP/C without heating and heated at 10W after 100 cycles. (c) Discharge profile at 0.5C of LMNO and LMNO-2LFP/C without heating and heated at 10W and 100W.

Understanding the interplay between Li insertion and Li plating in single graphite anode

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The potential safety hazards of lithium ion batteries (LIBs), as well as their capacity fade and long charging time, are major challenges that currently prevent the widespread adoption of electric vehicles. These effects are strongly correlated with lithium plating, a parasitic reaction on graphite anodes that competes with lithium intercalation when LiBs are charged at high rates or under low temperature. Li plating is known for depletion of the lithium inventory, cell shorting, and thermal runaway.

Addressing Li plating problem relies on material engineering and battery operation optimization. The efficacy of these approaches lies in the fundamental understanding of Li plating mechanism. Despite Li ion battery has been invented for 30 years, a systematic understanding on the onset and growth of Li in graphite anode is still lacking. Thermodynamics criterion requires the voltage of graphite to be negative vs. Li metal for Li plating to happen. However, in practice graphite is usually able to tolerate certain degree of negative voltage without plating. Such discrepancy necessitates the incorporation of kinetic factors. Several kinetic mechanisms have been proposed, which include electrolyte transport limitation and solid diffusion limitation. However, neither of them are validated experimentally on graphite electrode.

In this work, we test these hypotheses and elucidate the mechanism of Li plating, by investigating the interplay between Li intercalation and Li plating on a single graphite particle, using in-situ optical microscopy coupled with electrochemical test. The results show Li plating happens when the surface of graphite saturates, which shuts down the intercalation reaction. The saturation can happen much earlier than full lithiation of graphite particle due to solid diffusion limitation, resulting in severe under-utilization. The physical picture was discussed by analyzing the energy landscape of the two competing reactions and their kinetics. A theory was proposed, followed by a 1D simulation of the dynamics of Li insertion and Li plating. The discovery sheds light on directions and guidelines of materials innovation or electrode design for reducing the risk of Li plating and extreme fast charging.

The Effect of a Filler Type on the Electrical Percolation Threshold of a Biocompatible Neural Interface Composite

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Electrical stimulation as the way to treat neural tissue disorders has been known in medicine for the last decades [1]. Currently, deep brain stimulation (DBS) is a common tool to treat several neurological disorders, including chronic pain, depression, tremors associated with Parkinson's disease and epilepsy. One of the drawbacks of existing DBS technologies is the lack of the integration between electrode material and neural tissue, leading to foreign body reaction and inflammation. Therefore, current strategies are focused on the development of conducting coatings which could increase the biocompatibility of neural electrodes, while maintaining their high conductivity.

In our studies, we have chosen an aliphatic polyester as a biocompatible matrix, and we have loaded it with selected conducting fillers differing in size, conductivity and surface morphology, namely carbon nanotubes (CNTs), silver nanowires (AgNWs) and conducting polymer microspheres (CPMs). It is known that the addition of a conducting filler can significantly enhance the electrical properties of non-conducting polymers. Usually, the change in electrical properties is not linear with the content of a conducting filler. Hence, even a small amount of conducting filler can dramatically improve the conductivity of the composite material if only this amount is enough to form long range networks, called percolation paths [2].

To determine the minimum amount of conducting fillers that provides conductive behavior to polyester matrix, electrochemical impedance spectra (EIS) and cyclic voltammograms (CV) of composites were collected, and the corresponding charge storage capacities (CSC) were calculated. The percolation behavior of the composites was clearly seen from the changes in impedance and CSC, and was found to be highly dependent on the filler type. The lowest percolation threshold was found for CNTs (0.1 %), but the highest value of CSC (10.7 ± 0.3 mC/cm^2) and the lowest impedance (167 ± 10 Ω) were found for 10 % AgNWs. The results of our work clearly demonstrated the potency of AgNWs to be used as conducting fillers in composite coatings for neural electrodes. AgNWs were shown to form an extended uniformly distributed network within polyester matrix, resulting in advantageous electrochemical properties.

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Electroactive Organic Monolayers as Multifunctional Neural Coatings

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Rapid growth and development at the intersection of neuroscience, computer science, engineering and medicine has allowed the creation of revolutionary neurotechnologies to evaluate and treat nervous system disorders. Neural interfaces have become a major focus in current research in an effort to identify and develop novel approaches to augment human cognitive or sensory-motor functions, to interface with computer systems or to control external devices [1]. The implantation of metal electrodes may, however, lead to persistent inflammation – this is why intensive research efforts have been made to develop biocompatible coatings preventing implant-associated adverse effects [2]. The optimal interface should not only exhibit biocompatibility, conductivity, low interfacial impedance, high stability and high charge injection capacity, but it should also prevent glial scar formation and inflammation [3]. Therefore, the range of biomaterials that can be used in this specific application is limited.

Our aim was to improve the efficiency of neural electrodes through the design of a novel type of coatings based on electroactive monolayers. The objectives of our work included the formation of electroactive monolayers with the use of the electrochemical reduction of diazonium salts (Fig.1). The formation of monolayers was monitored in situ, with the use of electrochemical quartz crystal microbalance and cyclic voltammetry. The as-formed monolayers were extensively investigated in terms of their electrochemical properties (charge storage capacity, charge injection capacity, impedance characteristics, conductivity), surface roughness, mechanical stability and biocompatibility.

The results confirmed that the electrochemical methods can be successfully employed to form and further modify electroactive monolayers. The examination of as-formed monolayers showed the formation of a uniform coating being able to be further modified by electrochemical methods, e.g. surface-induced electropolymerization. Moreover, the monolayers were shown to enhance the growth of neural cells when compared with a bare surface of platinum. Furthermore, unmodified and electrochemically modified monolayers were shown to differ in terms of surface characteristics (roughness), leading to the differences in the interactions with cells.

Combining the advantageous physicochemical properties of monolayer coatings together with their high tailorability for specific needs, we expect that the electroactive organic monolayers could serve as promising materials not only for neuroprosthetic coatings, but also for a variety of applications in the field of molecular scaffolds and medical devices.

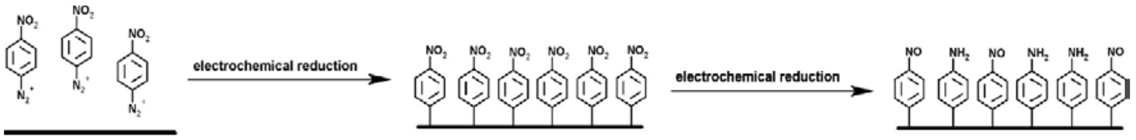

Fig.1. The schematic representation of a two-step process of the formation of a monolayer.

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Determination of membrane potential dependent structural changes in of a model of the outer membrane of Gram-negative bacteria

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Cell envelope of bacteria differs in the composition and structure from cell membranes of eukaryotes. Gram-positive bacteria contain one phospholipid membrane which is surrounded by a 20 – 80 nm thick peptidoglycan film. The cell envelope of Gram-negative bacteria has one of the most complex structure in nature. It is composed of two lipid bilayers. The inner membrane contains phospholipids. The inner membrane is separated from the outer membrane (OM) by a thin (7-10 nm) peptidoglycan layer. The two leaflets of the OM have a distinct composition. Lipopolysaccharides are present in the outer leaflet. They have a complex structure. Lipid A consists the amphiphilic fragment of each lipopolysaccharide. A core fragment of a lipopolysaccharide is bound to the lipid A molecule. It is subdivided into an inner and outer core. The inner core is bound to lipid A via rare sugars: 2-keto-3-deoxyoctulosonate (Kdo) and L-glycero-D-manno-heptose. The outer core is composed of few common sugar residues (hexoses and hexosamines). The polar head group of lipid A and core regions are negatively charged. Divalent cations (Ca^{2+}, Mg^{2+}) are coordinated to the phosphate, carboxylate and hydroxide groups of this rigid fragment of a lipopolysaccharide molecule. A large structural diversity of LPS combined with the complex supramolecular structure of the OM limit biomimetic studies of the cell membrane envelope of Gram-negative bacteria.

In this work Langmuir-Blodgett and Langmuir-Schaefer (LS-LB) transfers were used to deposit a multicomponent asymmetric lipid bilayer, mimicking the composition of the OM of Gram-negative bacteria, onto an Au(111) electrode surface. The inner leaflet is composed of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (POPE) whereas the outer leaflet contains di[3-deoxy-D-manno-octulosonyl]-lipid A (KLA). The capacitance of the model OM depends on the potential applied to the Au(111) electrode. At negative membrane potentials, the bilayer desorbs from the electrode surface. The potential-driven adsorption-desorption process is reversible. Molecular scale changes in the model membrane exposed to physiological electric fields were investigated using *in situ* polarization modulation infrared reflection absorption spectroscopy. The orientation of the lipid molecules in the asymmetric OM depends on the membrane potential. The hydrocarbon chains of both lipids POPE and KLA exist in a liquid state. The orientation of the acyl chains in POPE, in the inner leaflet, does not change as a function of the membrane potential. In contrast, the hydrocarbon chains in KLA change their average orientation as a function of potential, reaching the largest disorder at negative membrane potentials, proceeding the bilayer desorption from the Au(111) electrode surface. The polar head groups response also to membrane potentials. The orientation of the line connecting the two O atoms in the carboxylate group slightly change as a function of the membrane potential. The ester carbonyl groups in POPE and KLA lipids have a preferential parallel to the bilayer plane orientation, which is not affected by the membrane potential. Our results demonstrate that electric potentials cause significantly smaller changes in the packing and hydration of lipid molecules compared to pure phospholipid bilayers. To understand interactions of bacterial membranes with antimicrobial peptides or other antibiotics, biomimetic studies of realistic models of bacterial cell envelopes are required.

Choosing the right carbon is of vital importance for high performance Sb-based Na-ion batteries

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Electrodes based on alloying reactions for sodium-ion batteries (NIB) offer high specific capacity but require bespoken electrode material design to enable high-performance stability. This work addresses that issue by systematically exploring the impact of carbon properties on antimony/carbon composite electrodes for NIBs. Since the Sb surface is covered by an insulating oxide layer, carbon additives are crucial for the percolation of conductive pathways and to enable the electrochemical activity of Sb based anodes. Instead of using complex hybridization strategies, the ability of mechanical mixing to yield stable, high-performance Sb/C NIB electrodes is shown. This is only possible by considering the physical, chemical, morphological, and structural features of the carbon phase. A comparison of carbon nanohorns, carbon onions, carbon black, and graphite as conductive additives is given in this work. The best performance does not require a high or low surface area, and not a high or low heteroatom content. Instead, the best performance is obtained for electrodes displaying a homogenous distribution of carbon within the Sb matrix. The latter provides an optimum interaction between carbon and Sb and is best enabled by carbon onions. A remarkable rate performance is attained, electrode cracking caused by volume expansion is successfully prevented, and the homogeneity of the solid/electrolyte interphase is significantly improved as a result of it. With this composite electrode, a reversible capacity of 490 mAh/g at 0.1 A/g and even 300 mA/g at 8 A/g is obtained. Additionally, high stability with a capacity retention of 73 % over 100 cycles is achieved at charge/discharge rates of 0.2 A/g.[1]

Acknowledgments:
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Enhanced air-stability of argyrodite solid electrolyte for all-solid-state batteries

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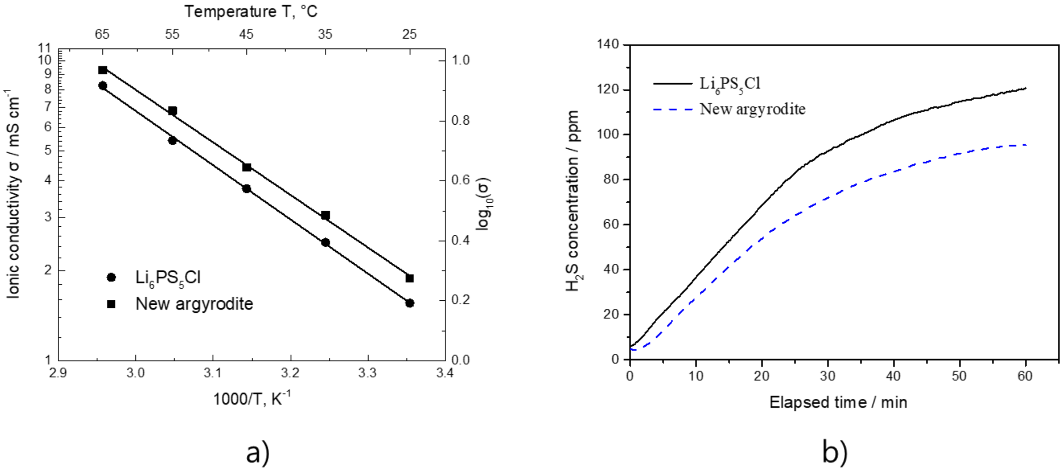
Over recent year, the range of Li ion battery (LIB) application has been rapidly extended to large scaled uses such as electric vehicles (EVs). This has driven demand for Li ion battery system that can offer higher energy density, higher current drain, and greater safety. All-solid-state batteries (ASB) have received great attention as a next generation power source due to its high energy densitsy with safe characteristics. Whole battery reactions are occurred in solid-state Li+ migration in ASB, therefore the well-contacted interfacial area is critical for battery performance. Solid electrolyte is key materials in ASB. Sulfide solid electrolyte is favorable to form a contact area effectively due to its elastic powder character compared to oxide. However, sulfide solid electrolyte is chemically unstable with humidity in air. It easily generates H_2S gas that is toxic and hazardous. Residual Li_2S and bridge sulfur in structure are known as main cause of H_2S generation. The ionic conductivity is also decreased by the decomposition of solid electrolyte by undesirable H_2S generation. Our previous works proposed the addtive such as zeolite and metal oxide as H_2S scavenger. H_2S gas generation and ionic conductivity after air exposure were greatly imptoved by introducing additive. In this study, we reports new argyrodite-type solid electrolyte that shows improved ionic conductivity at room temperature. The amount of H_2S gas generation was reduced for new arygrodite after exposured in moisture air (Rh50% for 60 min). Decease of ionic conductivity after air exposure is also suppressed. Electrochemical performance such as specific capacity and cycle performance is also improved for new argyrodite. The detailed results will be discussed at the meeting.



a) b)

Fig. a) Arrhenius plots of the ionic conductivity values of LPSCl and new argyrodite, b) amount of H2S gas generation from solid electrolyte during exposure to air (Rh 50%)

New Roles of Ion Selective Membranes for Capacitive Deionisation and Battery Desalination

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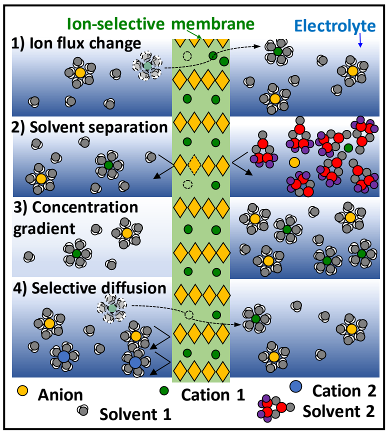

In a recent decade, a wealth of new electrochemical ion-separation technologies, such as capacitive deionisation (CDI) and battery desalination, have emerged as energy-efficient alternatives to conventional technologies.[1, 2] Relying on reversible electrochemical reactions as a driving force such as electric double-layer formation and insertion/intercalation, conversion type redox reactions, desired species such as metal and halide ions can be efficiently removed from feed solutions.[2, 3] Furthermore, large facilities based on these technologies can be coupled to grid-scale energy storage systems since the deionisation cell is essentially operated by electrical charging/discharging procedures.

For further development of these ion-separation technologies with reversible electrochemical reactions, the key challenges are to enhance removal selectivity, energy efficiency, operation stability, and production rate, and to reduce the environmental influence and the cost. While the majority of the work has been focused on electrode materials to achieve these requirements, ion-selective membranes have played their conventional role to improve ion removal efficiency. The letter approach, known as membrane CDI (MCDI), prevents the inefficient ion removal process by providing a guided direction for ion flux. Recently, various new roles of membranes have been explored for CDI and battery desalination technologies via innovative cell design and the use of advance new membranes.

Herein, we introduce the new roles of ion-selective membranes for ion-separation processes with reversible electrochemical reactions based on our recent scientific achievements. First, the traditional roles of membranes in terms of providing a guided ion flux will be discussed as well as its novel functions of changing the traditional direction of ion flux.[4-6] Second, we will introduce the new role of solvent separation with our proof of concept study demonstrating the feasibility of applying aqueous/organic bi-electrolyte configuration.[7] Third, we will present how the ion-separation performance can be enhanced by applying concentration gradient with the aid of ion-selective membranes in a multi-channel cell.[8, 9] Finally, we will show how ion-selective feature of the membranes can provide innovative solutions for ion separation technologies with a synergistic combination with the redox-active electrolytes.[4, 10]

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Analysis of Single-Phase Water-Management Signatures in Fuel-Cell Impedance Spectra

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Electrochemical impedance spectroscopy (EIS) is widely used for the characterization of proton-exchange-membrane fuel cells (PEMFCs) as it allows researchers to separate physical processes occurring at varying temporal scales [1,2]. The PEMFC impedance spectra often contain a low-frequency inductive loop that is attributed to the electrolyte hydration [2-6]. Since water management plays an important role in achieving high PEMFC performance, better understanding of the physical meaning of this inductive behavior will help in future fuel-cell design.

Developing physical insight by using equivalent circuits to analyze the impedance spectra [1,2] is difficult due to the oversimplification of the physical phenomena. Only a few multi-dimensional numerical models have been used to investigate the inductive behavior of fuel cells [3-5]; however, in-depth parametric studies of water transport were not performed.

In this work, the detailed transient 2D PEMFC model from our recent publication [7] is used to simulate and analyze fuel-cell impedance spectra. The model was thoroughly validated against in-house experimental polarization curves, ohmic resistance, and EIS data, as well as the recent experimental data for the humidity-dependence of the inductive loop [8]. The low-frequency inductive behavior of PEMFCs is shown to be directly affected by the water-transport mechanisms in the membrane and in the ionomer phase of the catalyst layers, including the finite-rate kinetics of water absorption/desorption by the electrolyte. Additionally, an ohmic-resistance breakdown of an in-operando fuel cell is performed with the model. The results indicate that the high-frequency resistance of the PEMFCs does not include the protonic resistance of the conventional carbon-based catalyst layers, while the latter is still significant in the overall ohmic losses.

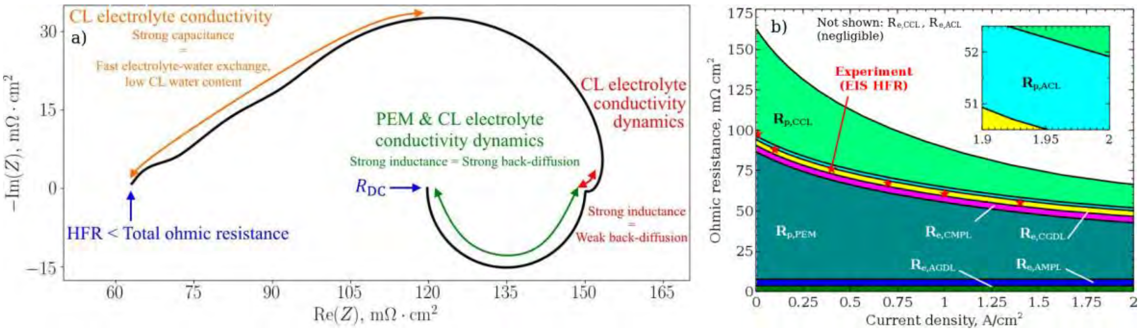

Figure: A PEMFC impedance spectrum simulated at 1 A/cm^2 (a) and ohmic-resistance breakdown (b).

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Electrochemical and surface analysis of biofunctionalized anodized zirconium to promote osseointegration

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Zirconium is a promising candidate for permanent implants both in orthopedic and dental applications due to its capability of promote the growth of new bone tissue with low cytotoxicity and excellent corrosion resistance [1,2]. Zirconium is covered in air or oxygenated media by a thin surface film of zirconium oxide, responsible of its outstanding *in vivo* and *in vitro* results [3,4]. Anodization represents an efficient route for surface modification that allows the surface design in the nano and micro scales fundamental for the improving implants performance [5]. In previous works, anodic growth of ZrO_2 surface films in phosporic acid resulted beneficial for implant osseointegration due to the modification of the topography and the chemistry of the surface, including P incorporation to the oxide film structure [1,2]. This, in turn, can induce the precipitation of Ca-P compounds on the surface. Furthermore, *in vitro* and *in vivo* tests have shown that the surface of ZrO_2 created by anodic oxidation at 60 V improves cell proliferation and the integration of the material into bone tissue [2,6]. In the past decade, numerous studies have focused on controlling the interaction between tissue and implanted materials by immobilizing functional biomolecules that could stimulate and interact with the extracellular matrix environment [7-9].

In this work, the effect of functionalization of anodized zirconium with a bioactive peptide (RGD) as potential manufacturing material for osseointegrable implants to stimulate early bone integration is presented. The surface modification was evaluated by surface methods including scanning electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Surface analysis shows the presence of ZrO_2 covering the surface. XPS shows the presence of the peptide on the surface after modification. Electrochemical tests were performed in simulated body fluid solution (SBF) in order to determine the effect of functionalization with the organic molecules on the corrosion resistance of anodized zirconium. Anodic polarization curves and electrochemical impedance spectroscopy results indicate that both anodized and functionalized with the RGD peptide surfaces present excellent corrosion resistance in SBF after 24 hours of immersion. EIS results evidences that both surfaces behave as non-ideal capacitors, characteristic of passive films on valve metals. These results demonstrate that the functionalization treatment with RGD peptide does not cause any detrimental effect on the anodic oxide formed on zirconium during anodization.

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Effect of Specific Cation Adsorption on CO_2 Electroreduction in Ionic Liquids

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Ionic liquids (ILs) have recently gained substantial attention as promising solvents for the capture and sequestration of CO_2 and as reaction medium for its electrochemical conversion into valued-added products. It has been reported that ILs can co-catalyze the electrochemical CO_2 reduction reaction (CO_2RR), in particular when Ag or Ag-based materials are applied as the primary metallic electrocatalyst [1]. Despite several attempts to explain the co-catalytic effect of ILs in CO_2RR, the mechanism is not yet fully understood. Recently, the co-catalytic effect was explained by stabilization of CO_2RR intermediate, CO_2 radical anion, with IL cations adsorbed on a Ag electrode surface [2]. In order to broaden this co-catalysis concept and to develop an in-depth understanding of the co-catalytic action of the IL, we present herein a comprehensive study on a number of electrode materials (Pt, Pd, Ag, Au, Bi, Pb, Sn, Ni, Mo, Fe, Zn, Cu, and glassy carbon) exposed to several ILs, differing in the chemical nature of their anions and cations (Fig. 1) [3]. The activity of the electrode/IL combinations towards CO_2RR is examined on the basis of cyclic voltammetry (CV) data recorded in Ar- (blankets) and CO_2-saturated ILs. The voltammetric experiments are further complemented by online gas chromatography analysis of the electrolysis products, demonstrating that CO is the main CO_2RR product for most of the electrode/IL combinations chosen. Based on our analysis we identify three major classes of electrode materials differing in their synergistic interaction with the IL cations and the in resulting CO_2RR activity: (i) non-active (CO_2RR is negligible in the potential range of IL stability), (ii) moderately active (CO_2RR is hindered and proceeds together with the cathodic degradation of ILs), and (iii) highly active (CO_2RR proceeds with nearly 100% faradaic efficiency). We also demonstrate that IL cations have a strong effect on the CO_2RR overpotential (Fig. 1a-c, compare data for [BMP][TFSI] and [BMIm][TFSI]). Moreover, the co-catalytic effect depends on the electrode material: $[BMIm]^+$ promotes CO_2RR on Ag and Sn more than $[BMP]^+$, while the situation is opposite for a Au electrode (Fig. 1a-c). Therefore, co-catalytic effect of ILs in CO_2RR is determined by specific IL cation adsorption, and only particular combinations of electrode materials and IL cations enhance the CO_2RR activity.

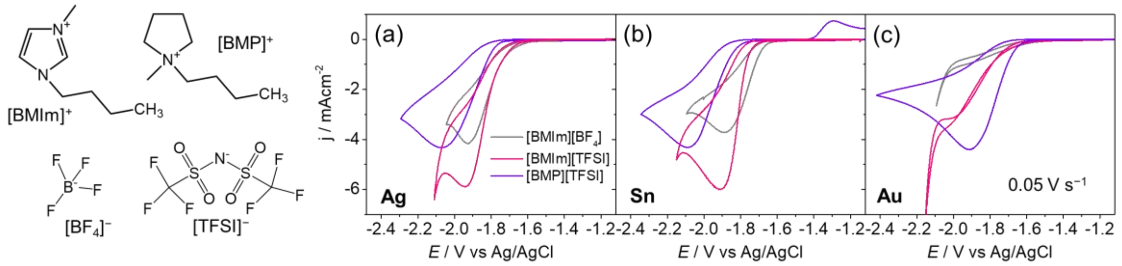

Figure 1. (Left) Cations and anions of ILs used in this work. (Right) Comparison of the CV fragments in CO_2-saturated ILs for the (a) Ag, (b) Sn, and (c) Au electrodes.

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Electrochemical sensors for iron detection in artificial water systems

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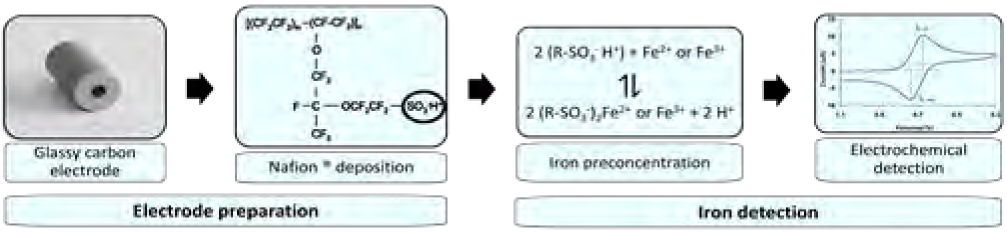
Iron is a very abundant chemical element naturally present in the Earth's crust [1]. It plays an important role and has major effects in environment (like in fresh and sea water), in industry (for instance in corrosion problems) or in humans (as it is implied in many biological or metabolic systems). Iron is mainly present as ferrous Fe(II) and ferric Fe(III) in aqueous media. However, Fe(II) is spontaneously oxidized in the presence of oxygen whereas Fe(III) is weakly soluble and forms stable complexes and precipitates at neutral pH [2]. Furthermore, the permissible values of iron concentration in drinking water is between 0.3 – 3 mg L^{-1} (i.e. $5.3\ 10^{-6} – 5.3\ 10^{-5}$ mol L^{-1}). Consequently, the assay of total iron at low concentration as well as the determination of iron speciation is of key interest and still represent an analytical challenge.

Many analytical methods have been developed in routine to detect and quantify iron in natural water involving chromatography, spectrophotometry, fluorescence, chemiluminescence and so on. However, all these techniques are expensive, bulky and time-consuming. Alternatively, electrochemical methods have been advantageously considered since they are low-cost, user-friendly, produce results in real time and can be used *in situ* [3-4]. If polarographic methods are currently not used anymore for evident toxicity reasons, mercury-free electrodes techniques based on adsorptive stripping voltammetry have been extensively developed these last ten years [5-6]. Nevertheless, these imply chelating agents including catechol or cupferron, thus making the procedure complicated and chemical-consuming.

In this work reagentless electrochemical sensors have been considered for the detection of Fe^{2+} and Fe^{3+}. Two amperometric sensors have been developed based on glassy carbon electrodes modified by deposition of a Nafion® cation exchange resin film containing sulfonic groups. Fe^{2+} and/or Fe^{3+} were pre-concentrated at open circuit conditions during 5-10 minutes, allowing ion exchange with protons. Electrochemical detection was then performed by cyclic or square wave voltammetry. In both techniques signals related to iron were recorded, the peak currents of which being proportional to Fe^{2+} and Fe^{3+} concentrations, respectively. Satisfactory calibration curves were achieved in the micromolar concentration range when analyzes were made in synthetic solutions. Limits of detection down to 0.1 and 0.01 µmol L^{-1} were reached for Fe^{2+} and Fe^{3+} respectively and the sensors exhibited a reproducible response for at least 15 measurements. Furthermore, accuracy was verified by comparing electrochemical results with ICP-OES analyzes. Finally, promising results obtained with real water samples from artificial circuits will be presented.



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Pressurized Heterogeneous Electrofenton Reactor for the Treatment of Hospital Effluents

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The presence of pharmaceutical compounds in hospital effluents is causing the emergence of bacteria resistant to antibiotics. These effluents have low biodegradability making them potential pollutants. At this point, electrochemical advanced oxidation processes (EAOPs) are an alternative clean and effective to conventional processes. Especially, electro-Fenton process has provided promising results for the removal of pharmaceuticals compounds [1], which involves the use of hydroxyl radicals to oxidize these contaminants. The mechanism of this process consists in-situ hydrogen peroxide electrogeneration via cathodic reduction of oxygen and the generation of OH^* via Fenton´s reaction.

The objective of the present work was the partial elimination of drugs to improve the biodegradability of these effluents using a microfluidic flow-through cell with a pressurized-jet aeration. It was also incorporated a fluidized bed of iron particles, to catalyse the decomposition of H_2O_2 into oxidizing species. Figure 1 shows an outline of the experimental set-up.

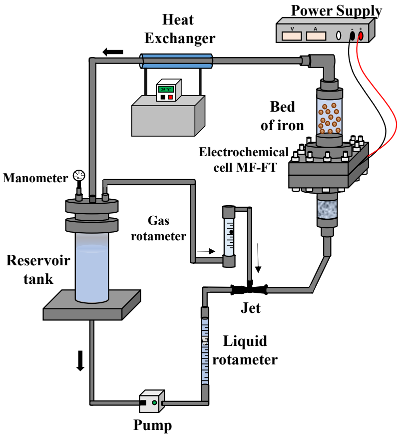

Figure 1. Experimental set-up

Tests were conducted using a 3D-Mixed Metal Oxide (MMO- $IrO_2Ta_2O_5$) as anode and a 3D titanium mesh with a deposition of Carbon Black and PFTE as cathode with different current densities (1 mA/cm^2, 5 mA/cm^2 and 10 mA/cm^2) and pressure ranged from 1 to 4 Bar. Previous experiments have shown that current density and pressure have an important role in the degradation of antibiotics.

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The role of water matrix on the removal of antibiotic-resistant bacteria by electrochemical oxidation

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The occurrence of antibiotic-resistant bacteria (ARB) in wastewater has become an important concern for today´s society because they are one of the main causes of deaths during the last years. This problem is more dangerous in sanitary facilities where the concentration of ARB is higher due to the different infections of hospitalized patients. Specifically, large concentrations of ARB can be found in urine since many of them are mainly excreted by this way. Therefore, hospital urine can be considered as a target effluent to treat for the removal of ARB before its discharge to sewage. In this context, it is necessary to develop environmentally-friendly and efficient technologies that allow to remove ARB from hospital urines, avoiding the formation on undesirable disinfection by-products (DBPs). One of the technologies that has been proven efficient for disinfection of urban treated wastewater is electrochemical oxidation [1]. This process consists of the production of large amounts of disinfectant species, mainly free and combined chlorine compounds, from the oxidation of the ions naturally found in wastewater. These species attack the microorganisms present in the effluent, causing their death and guaranteeing a persistent disinfection treatment. The process efficiency is clearly affected by the anode material, current density and wastewater composition. Hence, these are the main operating parameters that should be evaluated.

With this background, the present work aims the applicability of electrochemical oxidation as disinfection technology for hospital urines polluted with two different types of ARB: *Klebsiella pneumoniae* (gram-negative) and *Enterococcus faecalis* (gram-positive). Boron Doped Diamond (BDD) and Mixed Metal Oxides (MMO) were tested as anode materials during the electrodisinfection of hospital urines at current densities within the range 5-50 A m^{-2}. Likewise, the removal of ARB with BDD and MMO anodes was studied in urban treated wastewater at different current densities to evaluate the influence of the effluent composition. Results show that it is possible to attain a complete removal of ARB in both effluents, hospital urine and urban treated wastewater. The disinfection efficiency is higher during the process in urban treated wastewater. This behavior can be explained by the higher organic load of hospital urines. Specifically, this effluent contains not only inorganic ions and bacteria but also other organics such as urea, creatinine and uric acid in high concentrations. The oxidation of these compounds can compete with the removal of ARB, decreasing the disinfection efficiency. On the other hand, the formation of DBPs was discarded during the treatment of hospital urines whereas significant amounts of chlorates were detected in urban treated wastewater. This can be related to the higher nitrogen content of hospital urines that favors the production of large concentrations of chloramines instead the promotion of hypochlorite to other hazardous chlorine compounds in high oxidation state. These results reveal that it is more appropriate to remove ARB in hospital urine despite the lower efficiency since it is possible to avoid the formation of DBPs.

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Synthesis and characterization of textile electrodes coated with Pt nanoparticles on electrochemically reduced oxide: treatment of industrial effluents loaded with organic dyes

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Pollution of dyes is a great problem of the environment in many countries and frequently detected in watercourses and groundwater, and may have proven toxicity. The use of textile materials, as substrates for electrodes for dye degradation, offers many possibilities due to its mechanical properties, such as flexibility, and a high specific area. Moreover, graphene has attracted the attention of researchers due to its very high specific surface area (2630 m^2 g^{-1}) and the unique and outstanding mechanical and electrical properties **[1]**. That is why the main objective of this work was to study the behaviour of textile electrodes coated with reduced graphene oxide and platinum nanoparticles in the electrochemical treatment of wastewater containing dyes**[2].** Initially, we determined the adequate experimental conditions to obtain thin layers Pt nanoparticles, with good reproducibility of synthesis. The characterizations of material at the microscopic scale, using Field Emission Scanning Electron Microscopy **(FESEM)** and Energy-dispersive X-ray spectroscopy **(EDX)** have allowed us to deepen our knowledge on the material before his use, and to validate its structural stability after electrochemical treatment.

The degradation of Orange G dye was studied by anodic oxidation with Pt-RGO using sulphate as electrolyte. A significant decrease in total organic carbon (TOC), chemical oxygen demand (COD), and total nitrogen (TN) was obtained. The chromatography and the UV-Visible spectrophotometry assays indicated that decolourisation is obtained at a loaded charge of around 0.17 Ah L^{-1} which is associated with an electric power consumption of 1.28 kWh m^{-3}. These encouraging results were obtained at very low energy costs, allowing us to consider the possible application for wastewater treatments, in addition to existing treatments or directly to the source of pollution. The influence of the presence of chloride in solutions has been also studied.

Keywords: Dyes, Pt nanoparticles, textile materials; degradation, anodic oxidation

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Reaction Mechanism Investigation of Orthorhombic V_2O_5 as Positive Electrode Material for Aqueous Rechargeable Zinc Batteries

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Recently, aqueous rechargeable zinc batteries (ARZBs) have received much attention for application in large scale energy storage thanks to their advantages, such as low cost, sufficient abundance, and high safety[1-2]. Aqueous electrolytes have higher ionic conductivity (up to 1 S cm^{-1}) than that of non-aqueous electrolytes, resulting in a higher rate capability and lower activation energy for charge transfer[1]. Meanwhile, the usage of aqueous electrolytes can reduce the manufacturing costs of ARZBs due to their properties such as non-toxic, inflammable, and non-strict humidity control[3-4]. Moreover, Zn has a high specific capacity (820 mAh g^{-1}) and high volumetric capacity (5854 mAh cm^{-3}), making it promising as a negative electrode. Thanks to its high potential (-0.76 V vs. SHE), it can be directly used as a negative electrode in aqueous-based electrolytes. However, the lack of high-performance positive electrode materials and the heavy mass and large polarization of Zn^{2+} hinder the practical applications of ARZBs.

V_2O_5 is considered a promising positive electrode for ARZBs due to its typical layered structure and relatively high capacity. Despite its good electrochemical performance, the structural changes of V_2O_5 during electrochemical processes are still in debate. Three different viewpoints regarding the structural changes of V_2O_5 in ARZBs have been proposed so far: *(i)* Zhou *et al.*[5] reported the formation of a new phase $Zn_xV_2O_5$ upon Zn insertion into V_2O_5 via *ex situ* XRD. *(ii)* Zhang *et al.*[6] proposed the co-intercalation of hydrated Zn ions into V_2O_5 crystal structure based on the *ex situ* XRD, XPS, and TEM experiments. *(iii)* Chen *et al.*[7] reported that orthorhombic V_2O_5 underwent a phase transition to zinc pyrovanadate during the first discharge *via ex situ* XRD, Raman, and XPS. However, the electrochemical reaction mechanism of V_2O_5 in the above-reported works was investigated through *ex situ* techniques. The findings are in controversy with each other and detailed structural changes of V_2O_5 upon Zn-ion insertion/extraction are still missing. Moreover, non-equilibrium or intermediate species/states cannot be detected using *ex situ* studies while *in operando* studies can provide a more reliable understanding of the structural evolution of a battery material in “real time”.

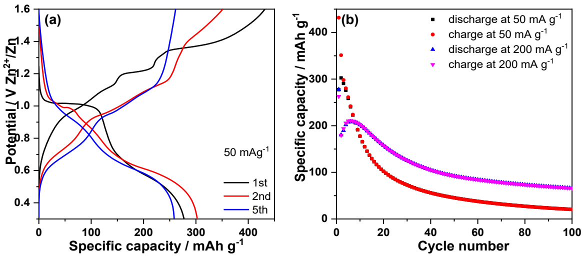

Figure 1 Discharge-charge profiles (a) and cycling performance (b) of V_2O_5 nanowires in 1 M $ZnSO_4$

Besides, it has been frequently reported that a mass of complex byproducts was produced/decomposed during the cycling of vanadium oxides in ARZBs. Interestingly, byproducts were not observed in the three works related to the study of V_2O_5 reported above. To better understand the electrochemical mechanism of V_2O_5 in ARZBs, *in operando synchrotron* characterizations are required. In the present work, orthorhombic V_2O_5 was prepared by a simple hydrothermal method. V_2O_5 nanowires exhibit an initial discharge and charge capacity of 277 and 432 mAh g^{-1}, respectively, at a current density of 50 mA g^{-1} (**Figure 1**). V_2O_5 undergoes quick capacity fading during cycling under both 50 mA g^{-1} and 200 mA g^{-1} current densities. The detailed structure evolution and reaction mechanism of V_2O_5 in ARZBs are studied *via in operando* synchrotron diffraction and X-ray absorption spectroscopy (XAS) together with *ex situ* Raman and X-ray photoelectron spectroscopy (XPS).

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N-doped Porous Carbons Derived from Tofu Solid Waste as Composite Electrodes for Lithium Sulfur Battery

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Actually, lithium sulfur (LiS) battery system is quite old battery technology since it has been studied since the 1960s. In addition, as a raw material, sulfur is very abundant and environmentally friendly, so it can offer economic benefits in the production cost of Li-S batteries. However, the problems in Li-S battery are very complex mainly due to poor kinetic properties, large volume expansions and dissolution of polysulfides into the electroylte made by aprotic solvent. All of these problems have caused a poor cycle properties and very severe capacity fading in Li-S battery. There are a lot of efforts devoted to enhance the performance of Li-S batteries, includes those are focusing on the sulfur cathodes, lithium anodes, new electrolytes and binders. In terms of the sulfur cathodes, many attempts have been proposed to enhance their electrochemical properties (discharge capacity, rate and cycling capabilities, and Coulombic efficiency) with the addition of heterogeneous materials. One of the most promising materials is the nanostructured carbons such as porous carbon, carbon nanotube or graphene. The nanostructured carbons own some remarkable chemical and physical properties which can contribute to the improved performance of sulfur cathodes in LiS battery system. Those kinds of properties include a highly porous structures provides a high surface area and pores for encapsulation of sulfur, a high electrical conductivity, good mechanical strength and an excellent inert property. N-doped porous carbon with high surface area, high nitrogen content and well connected porous structure has been synthesized from tofu waste by using hydrothermal carbonization and activation method. Due to the mesoporous structure, the carbon product has high surface area of large pore volume of 1.47 cm3 g^{-1} and mesoporous volume of 0.95 cm 3 g^{-1}. Attributed to the simultaneous effect of the mesoporous structure, high surface area and high nitrogen content ratio, the obtained porous carbon exhibits show excellent performance when used as composite cathodes along with sulfur for LiS battery. The carbon-sulfur composite was prepared by a melt diffusion method. The sulfur content in the composite was about 53.8 wt%, when utilized as cathode for LiS battery, the carbon-sulfur composite performs a high initial specific capacity of 1125 mAh·g^{-1} as well as 707 mAh·g^{-1} after 200 cycles at a current rate of 0.2 C.

Preparation of Microalgae Based Hard Carbons as Anode Materials for Sodium Ion Battery

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In recent years, sodium-ion batteries (SIBs) have emerged as promising candidate to replace lithium-ion batteries due to the low cost and high abundance of sodium (Na). The SIBs performance is essentially determined by the electrode materials applied. Hard carbon is a type of carbon that is relatively difficult to be graphitized and usually is synthesized from pyrolysis of polymer's precursors such as phenolic resins or epoxy resins. Hard carbon is highly irregular and disordered, and primarily consists of single-layered carbon atoms that are closely and randomly connected. Hard carbon is one component that plays an important role as an anode material in sodium-ion batteries. In this work, one of microalagae species, namely Chlorella pyrenoidosa was used to prepare hard carbons by using hydrothermal carbonizations and pyrolysis. The hydrothermal carbonization process was conducted in the autoclave at temperature of 200 °C for 24 hours. The obtained hydrochars were subjected to the pyrolysis process at pyrolysis temperature of 900 °C. The physical characterizations of hard carbons were done by Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) analysis. The as-obtained hard carbons were then used as anode materials for SIBs. Hard carbon can deliver the highest reversible capacity of 228 mAh g^{-1}, and show the high capacity retention of 95% at the current density of 100 mA g^{-1} after 100 cycles.

Electron Transfer and Ion Transport within Attoliter-Volume Nanopore Electrode Arrays

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Single entity electrochemistry, a rapidly developing field that tackles one of the most urging questions on the boundaries of modern electroanalytical methods and related disciplines. To effectively implement the single entity detection, the prior task for instrumentation is to fabricate electrode with a comparable size of a single entity that captures small signals with enough temporal and spatial resolution at a reasonable cost. Nanopore electrode, as a widely used nanoelectrode, not only addresses how electron transfer and ion transport in confined volumes, also seeks to understand how ultrasmall volumes impact electrochemical detection. Over the past years, we have observed and described several unusual effects enabled by working in confined volumes. In this presentation, I will describe a novel nanoelectrode developed by our group, *viz.* nanopore electrode arrays (NEAs). I will begin by discussing the design flow of NEAs and the critical points for the device fabrication and post-processing. Then, I will present studies showing significant signal amplification from highly efficient redox cycling and additional sensitivity and selectivity that arise from the migration-induced ion accumulation. Lastly, I will highlight practical applications using NEAs, including *in situ* molecular separation and detection with external stimuli, redox-based electrochemical rectification in individually encapsulated nanopores, and coupled sorters and analyzers for nanoparticles. These examples should provide significant motivation for listeners to pursue work in the area of nanoscale electrochemistry.

Electrodeposition of Rare Earth Metals and Their Alloys from a Dicyanamide Ionic Liquid

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Rare-earth elements (REEs) are one of the most important raw materials and are of great importance for the modern high-tech industry [1]. Low-temperature electrochemical deposition of REE-containing materials for the purpose of recycling and obtaining functional materials can provide a real alternative to the currently used high-temperature processes of molten salt electrolysis. The growing interest in ionic liquids (ILs) as media for electrochemical deposition of metals and semiconductors is due to their excellent physicochemical properties, including non-volatility, intrinsic conductivity, thermal and electrochemical stability [2]. The possibility of electrodeposition from IL-based solutions was demonstrated for various metals and semiconductors from the first to sixteenth groups of the periodic table [2]. However, studies on electrodeposition of REEs from ILs are scarce. Here, we present the investigation of electrochemical deposition of some chosen REEs in the 1-butyl-1-methylpyrrolidinium dicyanamide IL ([BMP][DCA]) at room temperature. Analysis of literature data shows that the dicyanamide ILs can be a proper choice as a medium for lanthanide deposition due to their relatively low viscosity (for [BMP][DCA], 50 mPa s at 293 K [3]) and good solubilizing ability [3]. The electrodeposition of REEs is studied on different single crystal electrodes with a controlled surface structure (Pt(111), Au(111), HOPG) as well as on a polished glassy carbon electrode. Cyclic voltammetry and chronoamperometry in the absence and presence of REE ions are used to identify REE-related electrochemical processes, while atomic force microscopy (AFM) is employed to characterize the deposit morphology obtained after potentiostatic polarization of the working electrodes. The voltammetric results demonstrate clear reduction of REEs at potentials more positive than reductive degradation of the IL (see the data for Eu deposition on Pt(111) in Fig. 1a). The AFM data confirm the REE deposition and reveal a strong dependence of deposit morphology on the substrate material and electrode potential, at which the deposit is formed (Fig. 1b-d). We also use the obtained data as a basis for studies on electrochemical deposition of REE–transition metal (TM) alloys from the dicyanamide ILs. As demonstrated in literature [4], TM with a more positive reduction potential can induce REE co-deposition with its reduction onset shifted to less negative potentials.

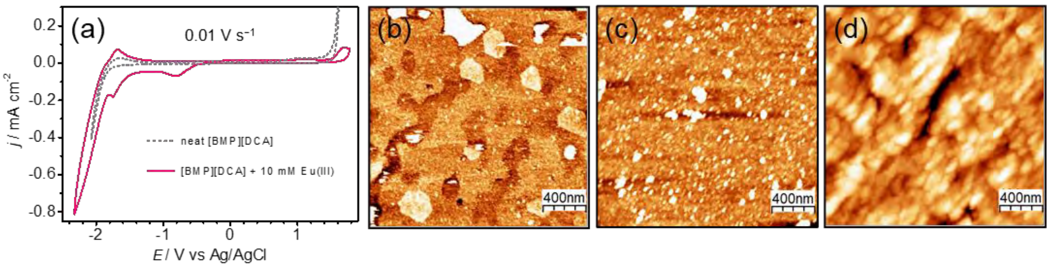

Figure 1. (a) Cyclic voltammograms of Pt(111) in pure [BMP][DCA] and in the presence of 10 mM Eu(OTf)$_3$. (b-d) AFM images of Eu deposits formed at different potentials: (b) -1.0 V, (c) -1.5 V, (d) -2.0 V) for 1200 s. The morphology changes from quasi-2D triangular or hexagonal islands to a compact granular deposit, depending on the overpotential.

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Unravelling the Capacity Fading Enigma of Spinel $Li_xMn_{2-y}Ti_yO_4$ by using Distribution of Relaxation Times (DRT)

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The demand for high capacity and inexpensive batteries is increasing rapidly with the upcoming energetic needs of an ever-increasing population, especially in the transportation sector. Spinel-type $Li_xMn_{2-y}Ti_yO_4$ cathode materials have been proposed as an alternative to the more expensive and toxic $LiCoO_2$ for Li-ion batteries [1]; however, stability issues persist [2] and the interaction between the active material and electrolyte at potentials below 3 V vs. $Li|Li^+$ is still a matter of discussion. We present an analysis of electrochemical impedance spectroscopy (EIS) using distribution of relaxation times (DRT) [3] as a method to reveal new insights regarding the capacity fading of $Li_xMn_{2-y}Ti_yO_4$ cathode materials.

A facile and improved sol-gel method was used to synthesised optimised $Li_xMn_{2-y}Ti_yO_4$ while maintaining nanostructured features. The stoichiometry $LiMn_{1.8}Ti_{0.2}O_4$ exhibited the best initial specific capacity (215 mAh g^{-1}) at 30.8 mA g^{-1} in a cycling window potential of 4.6 – 2.0 V vs. $Li|Li^+$. The incorporation of Ti increased the number of Li^+ diffusion pathways in the structure; adding Ti to replace a '*y*' amount of Mn in the spinel, i.e. $Li_xMn_{2-y}Ti_yO_4$ improves the specific capacity of the cathode materials by allowing both transitions, $Mn^{4+}|Mn^{3+}$ and $Mn^{3+}|Mn^{2+}$, to take place [1].

The effect of Ti incorporation and the underlying degradation processes during cycling were studied by cyclic voltammetry, cycling and electrochemical impedance spectroscopy (EIS), the latter was analysed by widely used equivalent electrical circuit and the more recent method of distribution of time constants (DRT), see Fig. 1. Cathode materials were also characterised at different cycling stages by XRD, Synchrotron XRD and SEM. Additionally, cathode materials were characterised by XPS, Raman and BET surface area. The results showed a clear indication of undesired structure modifications when the transition $Mn^{3+}|Mn^{2+}$ occurs, i.e. characteristic feature of topotactic two-phase reaction, and formation of irreversible tetragonal phase of the spinel which increases the charge transfer resistances at the active material | electrolyte interface. The presence of Ti did not inhibit completely undesired structure transformations, even after several strategies were implemented, e.g. addition of HF scavengers, different calcination temperatures and active material:binder ratios. A comparison between equivalent electrical circuit and DRT analysis is also presented. The investigation here offers a better understanding of the cathode materials and their correlations with electrochemical properties, which are of utmost importance for future researches on reaction kinetics and Li^+ transfer mechanisms in Li-ion batteries.

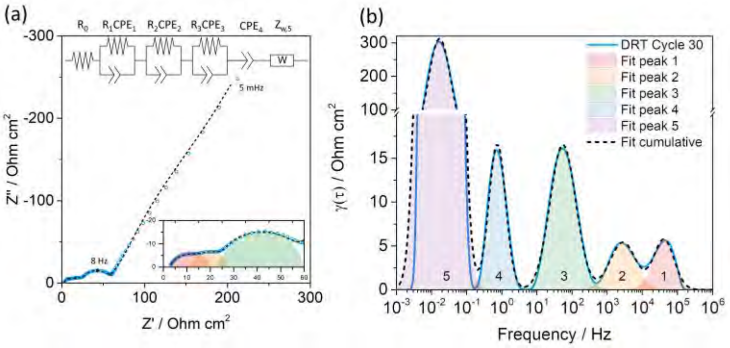

Fig. 1. (a) Nyquist plot of impedance spectra of $LiMn_{1.8}Ti_{0.2}O_4$ | 1.2 M $LiPF_6$ EC:DMC 1:2 | Li recorded at 4.0 V vs. $Li|Li^+$ after 30 cycles through a window potential of 4.6 – 2.0 V vs. $Li|Li^+$, (b) Computed DRT spectra and respective deconvoluted peaks.

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Theoretical Analysis of the Oxygen Reduction Reaction Limited by Surface Diffusion at a Rotating Ring-Disk Electrode

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The oxygen reduction reaction (orr) is the limiting process for power production in many electrochemical devices, like proton exchange membrane fuel cells and metal-air batteries. High orr rates in these devices can be attained with high active area cathodes based on catalyst nanoparticles supported in a porous matrix. In their reaction path, oxygen molecules diffuse in the gas and electrolyte phases until they arrive at the pores walls where they may interact with an active catalyst center or an inactive site. In the second case, orr may proceed either by successive desorption/adsorption steps until arriving at a catalyst center, or by surface diffusion towards a nearby catalyst site. The later may be the principal path with a low density of catalyst sites and sufficient surface diffusivity.

In this communication, a previously developed surface diffusion model [1][2][3][4] is applied to the orr at a dispersion of catalyst centers. The orr mechanism is depicted in Fig. 1a. The oxygen molecule adsorbs reversibly (k_1, k_2) on the supporting area by electrochemical or chemical reaction, where it may be partially reduced to hydrogen peroxide (k_i), or diffuse towards a catalyst center for complete reduction.

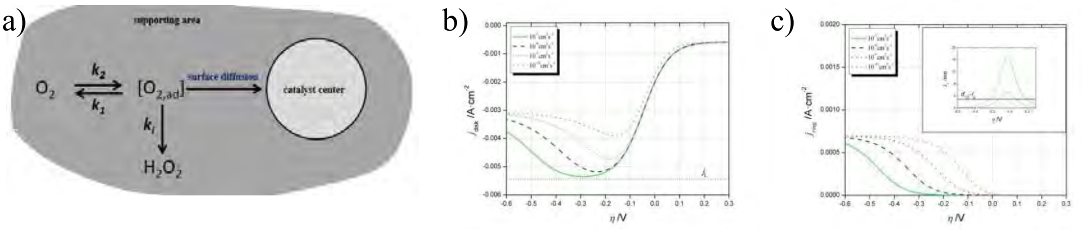

Fig. 1. a) Scheme of the orr mechanism mediated by surface diffusion. b) Disk current and c) ring current densities for orr on a dispersion of catalyst centers, under surface diffusion limitation, at four surface diffusivities. Inset in c: diffusion length as a function of overpotential (η). Overpotentials in b and c are referred to the electrosorption/desorption potential.

The model provides analytical expressions for the currents at a rotating ring-disk electrode, including disk (Fig. 1b) and ring (Fig. 1c) current densities as a function of surface diffusivity and parameters of the catalyst dispersion. Surface diffusivity is characterized by a diffusion length (λ_s), which depends on reactivity and overpotential (Fig. 1c, inset). The disk current may show a slope at high overpotential and/or a peak when maximal surface diffusivity is attained (Fig. 1b). Low surface diffusivity increases hydrogen peroxide reaction probability as observed in the ring (Fig. 1c). The analytical model shows how the efficiency of an electrode improves by increasing the surface diffusivity over supporting areas, which has high technological interest in the search for low catalyst loading electrodes.

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Tuning Of Photoelectrochemical Activity of Nanostructured WO_3 Films Through Modification of Sol-Gel Synthesis Procedure

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Photoelectrochemical (PEC) water splitting is considered as one of the most promising technologies in clean and renewable energy production. Numerous semiconductor materials have been intensively studied as photoelectrodes in PEC systems. Among them tungsten trioxide (WO_3) nanomaterials have received considerable attention due to the ability of capturing 12% of the solar illumination, band gap energy of around 2.5-2.7 eV, high crystallinity, moderate hole diffusion length, good chemical stability, low cost and low toxicity [1].

In this study, nanostructured layers of WO_3 on fluorine-doped tin oxide (FTO) substrate were formed by sol-gel method. Six different reductants were used to investigate their influence on photoelectrochemical activity and properties of WO_3 photoanodes. Peroxytungstic acid was synthesized using sodium tungstate (Na_2WO_4 x $2H_2O$), HCl and H_2O_2 as precursors and $(NH_4)_2C_2O_4$ as capping agent. Subsequently, methanol, ethanol, propanol, isopropanol, butanol or acetic acid was added separately as reductant, which slowly and controllably reduced peroxotungstates to form uniform and ordered $WO_3 \cdot H_2O$ films on FTO under soft water bath conditions at 85°C. After coating procedure, samples were annealed at 500 °C for 2 h with heating rate of 1°C/min to obtain a crystalline nanostructured WO_3 films and to remove residual carbon. The crystallographic structure of the calcined WO_3 films was characterized by X-ray diffraction (XRD) and photoelectrochemical behaviour of the samples was investigated by cyclic voltammetry (CV) (Fig. 1).

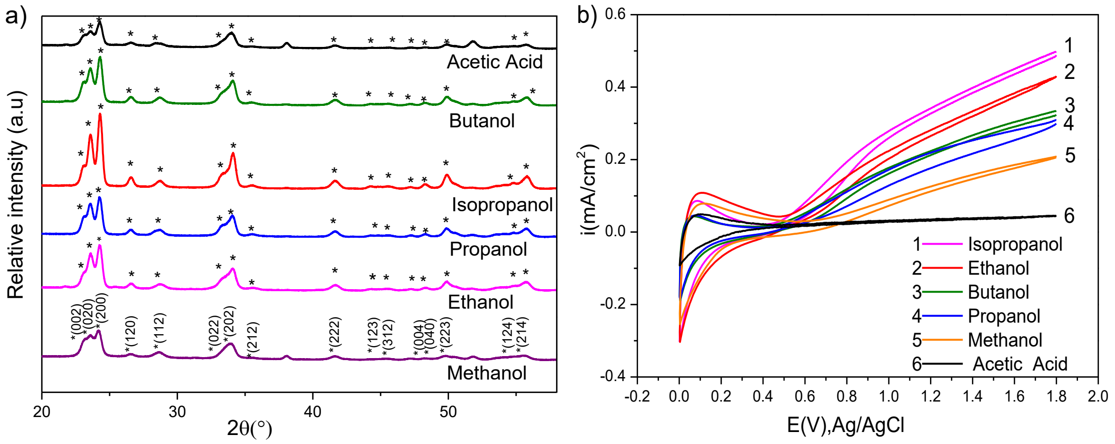

Fig. 1. a) XRD spectra of sol-gel derived WO_3 films formed using different reductants, b) cyclic voltammograms of the same films in 0.5 M H_2SO_4 solution, 50 mV s^{-1}, illumination P ~ 100 mW cm^{-2}

Fig.1a shows the XRD patterns of WO_3 samples formed using six different reductants. Films formed with isopropanol have the most intensive peaks in the whole range of 2θ which is attributed to the highest crystallinity. Cyclic voltammograms of FTO/WO_3 photoanodes recorded in 0.5 M H_2SO_4 under illumination represent typical response of WO_3. Using isopropanol as a reductant in the reported synthesis has been found to be the most effective route to increase the photoelectrochemical activity of WO_3 photoanodes, as these films showed the highest photocurrent density at 1.8 V (Fig. 1b). Photoelectrochemical activity of FTO/WO_3 electrodes prepared with six different reductants decreased in the following order: isopropanol > ethanol > butanol > propanol > methanol > acetic acid. Correlation between PEC activity and morphology, structure, phase composition of sol-gel derived WO_3 films will be discussed at the conference.

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Interactions between Oligonucleotides and Daunorubicin, Doxorubicin and Their Formamidino Derivatives Studied by Voltammetric and Spectrometric Methods

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Anthracyclines, such as doxorubicin (DOX) and daunorubicin (DAU), are anticancer drugs widely applied in therapy because of their cytostatic and cytotoxic activity [1,2]. Although they are very useful in chemotherapy, they reveal high toxicity inducing i.e. cardiac effects, gastrointestinal and hepatic effects, as well as bone marrow suppression and secondary malignancies [3]. For these reasons, seeking novel compounds with better biological properties is extremely important.

A new group of anthracycline derivatives has been synthesized [4,5]. In obtained formamidino anthracycline derivatives, the $–NH_2$ group in the daunosamine moiety was replaced by the amidine group ($–N=CH–NR^1R^2$) containing the rest of cyclic secondary amine ($–NR^1R^2$), a rest of morpholine or hexamethyleneimine. The first part of our studies on novel derivatives of anthracyclines have shown that daunorubicin and its two formamidino derivatives interacts differently with DNA chains containing GC and AT base pairs [6]. However, we have broadened our researches including doxorubicin and its derivatives, as well as using other spectrometric methods.

The purpose of the presented work was to investigate the interactions of DAU, DOX and its formamidino derivatives with oligonucleotides using voltammetric and spectrometric methods. They were investigated by monitoring changes in the UV-Vis and the Circular Dichroism spectra of the anthracyclines interacting with oligonucleotides in the solution, as well as by monitoring the changes in redox properties of oligonucleotides interacting with anthracyclines on the surface of screen-printed graphite electrodes by square wave voltammetry (SWV).

Our observations point to changes in DNA conformation caused by its interactions with anthracyclines and to dependence of these interactions mainly on two factors: the DNA sequence and the detailed structure of the daunosamine moiety of anthracycline. The influence of these factors on the interactions is discussed.

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Development of Acid-Base Flow Batteries for Renewable Energy Storage: Reversible Bipolar Membrane Electrodialysis

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Acid-base flow batteries (ABFBs) are receiving increasing attention due to their promising advantages for low-cost, utility-scale energy storage [1]. By using bipolar membranes in addition to cationic and anionic membranes, the concentration gradient across the key boundary can be increased, providing higher voltages than conventional reverse electrodialysis systems using concentrate and dilute water streams. During the charge process, water is dissociated into an acid and a base at the bipolar membrane. During discharge, a spontaneous neutralization takes place, generating electricity as a result of ionic transport processes. ABFBs use extremely low-cost and abundant reactants and the cell stacks have no bipolar electrodes (in contrast to redox flow batteries), but instead mesh separators and two monopolar electrodes [2]. ABFBs are closed systems, recirculating the electrolytes between their respective tanks and the stacks. As a result, the purity of the solutions can be guaranteed, eliminating problems such as 'up-hill transport' and biological fouling. The main challenges consist in the development of cost-effective membranes with very high selectivity in order to prevent capacity loss [3], and in the substitution of the inefficient water electrolysis taking place at the electrodes with the interconversion of fully reversible redox species.

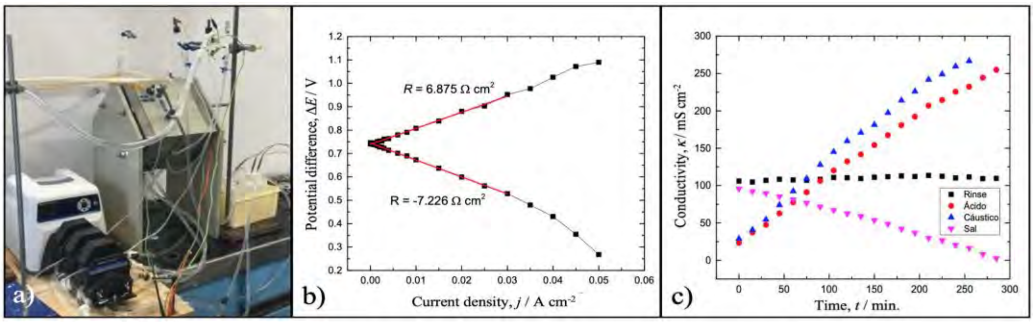

Figure 1. ABFB based on bipolar electrodialysis. a) Experimental arrangement with a 100 cm^2 cell and Luggin capillaries. b) Potential difference across an individual bipolar membrane during charge and discharge. c) Conductivity *vs.* time of the acid, alkaline, saline and *rinse* electrolytes during charge.

This work describes the advances made at the National Institute of Electricity and Clean Energy (INEEL) towards the development of ABFBs. As shown in Fig. 1a), an experimental arrangement with 5 L tank capacity per electrolyte controlled by a 30 A battery analyzer has been established for the study of individual membranes, unit cells and stacks. Performance and efficiency has been studied by OCP monitoring, polarization curves and by the measurement of conductivity and concentration of the electrolites during charge and discharge; see Fig. 1b). and Fig. 1c). Cross-over of ionic species and pressure drop over the mesh spacers have been also studied [4], with more advanced electrode and stack designs on the work.

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Thickness Uniformity of Nickel Coatings Deposited on Mild Steel from a Watts Bath Using a Tailored 3D Printed Flow Cell

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Electrochemical flow cells provide a well-defined experimental environment for applied electrochemistry, given the possibility of controlling both current/potential distribution and mass transfer conditions [1]. Recently, innovative uses of these cells beyond the classical conversion of ions in solution have been proposed, involving novel design-optimization processes [2], and the electrodeposition of composite coatings in tailor-made flow cells [3]. Nickel coatings prepared by electrodeposition are of paramount importance in many technical applications. Given the two-phase composition of nickel baths for composite coatings and the need to achieve a high dispersion of particles, it is desirable to produce the coatings under reproducible hydrodynamic conditions and current/potential distributions [4].

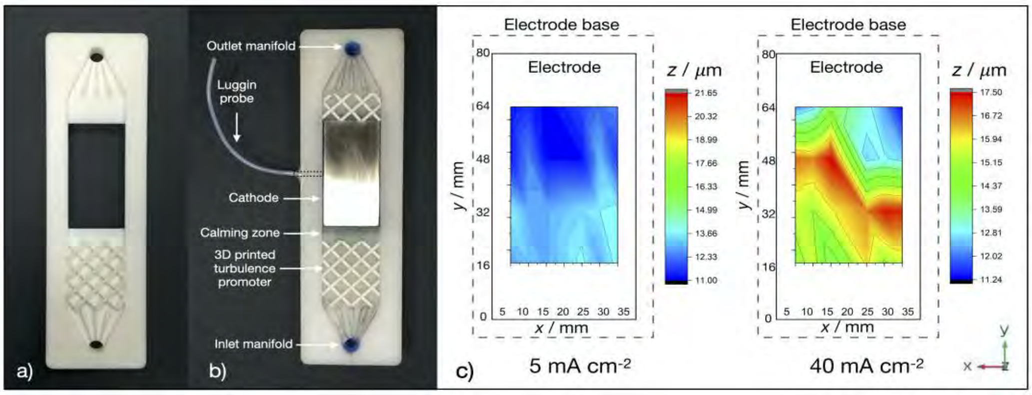

Fig. 1. Ni coatings produced on mild steel using a 3D-printed flow cell with a controlled hydrodynamic environment. a) 3D-printed frame and turbulence promoter. b) Components of the cathodic half-cell, showing a mild steel electrode. c) Coating thickness at the cathode surface for two current density values.

This work presents an analysis of the thickness uniformity of nickel coatings produced on mild steel substrates in a tailor-made flow cell by electrodeposition from a Watts bath. SEM images of cross-sectional samples of the coatings at different locations of the work pieces were collected and used to produce thickness maps. The results suggest that coatings prepared in this way can have a thickness variability below ±2 micrometres at relatively low current densities of 5 mA cm^{-2}. The coatings were less uniform at higher current densities of 40 mA cm^{-2}, displaying a variation of ±6 micrometres.

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Manganese Dioxide Film for Supercapasitors

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Manganese dioxide (MD) due to its electrochemical properties and availability is a promising material for use in supercapacitors (SC). There are many modifications of MD and not all of them have the necessary activity. As a modifying agent, we used iron to obtain a MD film with properties acceptable for SC. MD films on the platinum surface were obtained by the electrochemical method at room temperature from acidic solutions of manganese sulfate with the addition of Fe(II) or Fe(III). The addition of iron increased the film capacity, improved the shape of the cyclic voltammogram, and enhanced cycling stability. In order to elucidate the mechanism of iron incorporation into the MD film, the iron-free film obtained was anodically polarized in 0.5 M Na_2SO_4 at a potential of 1.2 V (all potentials were given vs silver chloride electrode). Then, Pt/MnO_2 electrode was kept in a solution containing only Mn(II), Fe(II), or Fe(III), and after washing in distilled water, the anode voltammogram was recorded in a solution of 0.5 M Na_2SO_4. When the electrode was preliminary kept in a Mn(II) solution and washed, an anode current peak was observed in the region of the electrodeposition potential of MD in 0.5 M Na_2SO_4 solution. We explained this behavior by the chemisorption of Mn(II) ions on the surface of MD:

$$MnO_2 + [Mn(H_2O)_6]^{2+} \rightarrow MnOOH[Mn(H_2O)_5OH]^{2+}_{ads.}$$

Afterwards, when the polarization curve was taken in Na_2SO_4 solution, the resulting particle was oxidized to MD. When the electrode was kept in a Fe(II) solution, a similar chemisorption of its ions on the surface of the MD occurred with the formation of Fe(III) and Mn(III). Therefore, the oxidation current of Mn(III) was observed on voltammogram, but the peak was less because less amount of Mn(III) was formed during the chemisorption of Fe(II). Keeping Pt/MnO_2 electrode in a Fe(III) solution did not lead to the formation of Mn(III), therefore, anodic peaks were not observed on the polarization curve. However, Fe(III) ions are adsorbed, without charge transfer, on the surface of the MD and thus pass into its structure. This conclusion is confirmed by the calculation of the current efficiency of the MD by the amount of consumed electricity for electrodeposition and the electrochemical dissolution of the films. The current efficiency of iron-free MD was 97%, doped with Fe(II) - 83%, and doped with Fe(III) - 110%. During the electrochemical dissolution of the film, part of the electricity was also spent on the reduction of Fe(III). Therefore, the current efficiency of the MD film exceeded 100%. The film capacity was calculated by the equation $C=I\Delta t/\Delta Vm$.

The best results were obtained by electrodeposition of a film in the presence of Fe(III). The capacity increased if the film was preliminarily polarized at a potential of 1.2 V in 0.5 M Na_2SO_4 and increased even more when it was then kept in a solution of 0.005 M $MnSO_4$. The specific capacity of a 70 nm thick MD film doped with Fe(III), preoxidized at a potential of 1.2 V in 0.5 M Na_2SO_4 and kept in a Mn(II) solution was 470 F/g.

ACKNOWLEDGMENT

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Electrochemical Pen and Paper – a New Approach to Ion Transfer Voltammetry

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Ion transfer has been explored directly for the detection of a large number of analytes but taking the technique out of the laboratory has been hampered by the mechanical sensitivity of the interface. A common approach to ensure a more stable organic-aqueous interface is also using gelled organic or aqueous phases, [1] but we recently showed that both phases can be stabilised in the cellulose matrix of paper [2].

Figure 1 Photo of the Electrochemical pen and paper device.

Here we combine a paper-stabilised aqueous phase with a gelled organic phase. The organic phase is held in a pen-like device comprising a glass-tube sealed with a porous plastic membrane in one end. Measurements are performed by pressing the pen against the paper. We demonstrate that the device functions as expectedly by measuring facilitated transfer of small inorganic ions. But we also show unique capabilities by "dip and pick" pre-concentration, where a sample is concentrated in the gel from several spots on the paper and then measured through stripping voltammetry.

Finally, we show that the EC pen can be used for electrochemical detection of proteins chromatographically separated in a paper-based flow channel. In this way we can get a direct electronic readout without the need for protein staining.

We envision that the concept of the electrochemical pen will move liquid-liquid analysis closer to practical application, where a sample can be spotted on paper or collected by swabbing and then measured using the pen device.

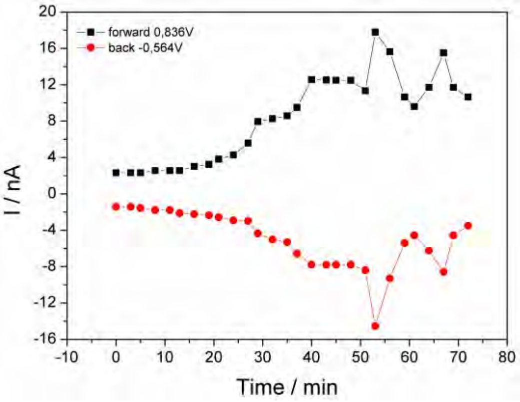

Figure 2. Electrochemical chromatogram. Dependence between the current and time plotted for chosen forward and backward sweep potentials for 5µl of Lysozyme and BSA mixture injected into the flow system.

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Effect of the synthesis route of platinum group metal-free catalysts for oxygen reduction reaction on microbial fuel cell performance

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Microbial Fuel Cell (MFC) belong to the larger category of bio-electrochemical systems (BES). MFCs oxidize organics on the anode and on the cathode an oxidant is reduced. Among several oxidants, oxygen is the most used due to the large availability in the atmosphere and it does have high reduction potential. Due to its sluggish kinetics and low concentrations of reagents, oxygen reduction reaction (ORR) is one of the main bottlenecks the system, therefore several investigations have been conducted in order to improve the performance.

At the cathode, in order to accelerate the reaction kinetics, a catalyst is used. Diverse biological, enzymatic and inorganic catalysts were adopted. Biological catalysts require high overpotential to operate. Enzymatic catalysts are very active but they are expensive and not durable in harsh environment. Inorganic catalysts are therefore the most used. This category can be divided in other three sub-categories: i) platinum group metal (PGM); ii) carbonaceous based; iii) platinum group metal-free (PGM-free) containing transition metal. PGM catalysts are expensive and are prone to get inactivated when in contact with pollutants. Carbonaceous based catalysts are cheap and durable but operates at high overpotentials. PGM-free composed by a transition metal (Fe, Co, Ni, Mn, etc) coordinated with nitrogen in pyridinic environment over a carbon backbone structure are the most promising.

In this work, the effect of pyrolysis process steps during the fabrication of Fe-N-C catalyst on: i) surface chemistry; ii) electrocatalytic activity towards ORR; iii) MFC performance were studied. Fe-N-C was synthesized using sacrificial support method (SSM) technique. The pyrolysis process followed six steps: 1) precursors mixing with silica; 2) first pyrolysis in reducing atmosphere (hydrogen rich); 3) ball milling of the obtained catalyst; 4) silica template etching using HF; 5) second pyrolysis in reducing atmosphere (ammonia rich); 6) ball milling.

The surface chemistry of the Fe-N-C catalyst varied after the high temperature processes and after the acid washing. The electrocatalytic activity was studied through rotating ring disk electrode (RRDE) experiment showing an improvement in the half wave potential and limiting current after each pyrolysis step. Performance in MFC were also evaluated. Particularly, power density was measured to be 167 ± 2 μWcm^{-2} when the catalyst subject to first pyrolysis was used. The power density increased after ball milling and silica etching measuring 181 ± 8 μWcm^{-2} and 185 ± 3 μWcm^{-2}, respectively. The second pyrolysis improved more importantly the power density produced, that was recorded to be 214 ± 5 μWcm^{-2}. The final ball-milling occurring after the second pyrolysis did not improved the performances that remained approximately stable at 212 ± 3 μWcm^{-2}. The change in catalyst surface chemistry was also related to the increase in ORR electrocatalytic activity and overall MFC performance.

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Electropolishing of biomedical Ti-alloy in eco-friendly deep eutectic solvent Ethaline

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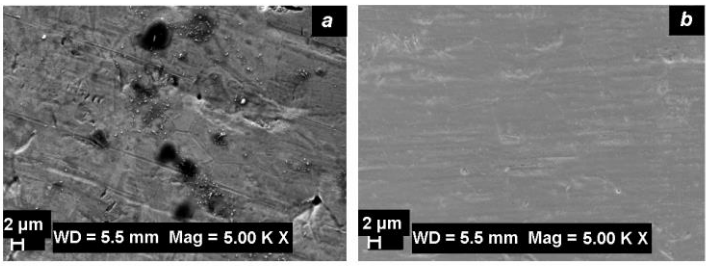
Titanium and its alloys are widely used to produce biomedical implant devices, since they combine high strength, inert behavior and low elastic modulus close to the bone elasticity, corrosion stability and good biocompatibility. However, commercial titanium and its alloys do not meet high requirements for biomaterials and medical equipment without preliminary special treatment of their surfaces (mechanical, chemical or electrochemical). The electrochemical surface treatment (electropolishing) is one of the most efficient methods of improving surface morphology and corrosion characteristics, but most common polishing electrolytes for the electropolishing of Ti and Ti-alloys are based on concentrated acidic solutions that often contain toxic additives, which create danger for the environment and human health.

In the present work, a deep eutectic solvent, Ethaline, was used as an environmentally friendly electrolyte for the electropolishing of Ti-based alloy (98.2% Ti, 0.30% Al and 1.50% C). Ethaline, a eutectic mixture of choline chloride (vitamin B4) and ethylene glycol, can be considered as a promising alternative to "conventional" electropolishing electrolytes. A unique combination of such properties of this deep eutectic solvent, as high viscosity and relatively high electrical conductivity, allows conducting electropolishing procedure under diffusion control, providing highly efficient surface leveling and improving corrosion resistance.

We established the optimal conditions for electropolishing of biomedical Ti-based alloy in deep eutectic solvent Ethaline as follows: the electropolishing potential of +3.0 V, the treatment duration of 30 min and the electrolyte temperature of 25 °C. It should be noted that the best results of electropolishing can be achieved by using Ethaline-based bath at ambient temperatures, where as common aqueous electropolishing electrolytes for the treatment of titanium require the use of either very high or very low temperatures. As shown in Figure, electropolishing in Ethaline contributes to a noticeable improvement in surface morphology. After electropolishing, the surface of Ti-based alloy samples exhibit the reduction in the amount of surface defects that are dissolved during anodic processing. The results of AFM analysis showed that a decrease in the surface roughness by more than 30% is observed after electropolishing.



SEM images of unpolished (a) and electropolished (b) Ti-based alloy (electropolishing was carried out in Ethaline at E=3 V, τ=30 min, and t=25 °C).

The linear polarization measurements revealed that electropolishing in Ethaline affect not only surface appearance and surface roughness, but also corrosion resistance (in NaCl aqueous solution). Electropolished samples of Ti-based alloy showed an enhanced corrosion resistance as compared with unpolished ones. The results of EDS measurements demonstrated that improved corrosion resistance after electropolishing may be associated with changes in both the surface morphology and surface chemical composition of Ti-based alloy.

Thus, deep eutectic solvent Ethaline can be considered as an available, eco-friendly and cheap electrolyte for the high-efficient surface treatment of biomedical titanium alloys that allows improving their surface appearance, surface roughness, corrosion properties and wettability.

Development of Graphene-Based Supports for Direct Methanol Fuel Cells.

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Palladium catalysts supported by graphene oxide, reduced graphene oxide, n-doped graphene oxide and reduced n-doped graphene oxide have been synthesized in this study. The graphene oxides and their reduced counterparts were obtained through modified hummer's method and thermal reduction using hydrazine hydrate, respectively. The catalysts were synthesized using modified polyol method. The structures were examined using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) for the prepared supports and prepared catalysts respectively. The FTIR showed that the surface of the supports exhibit oxygen containing functional groups (carboxyl, nitrosyl and hydroxyl) which serve as the anchor sites for metal deposition while the XRD confirmed that the catalysts exhibit face-centered crystal structure. High Resolution Transmission Electron Microscopy (HR-TEM) image showed spherical and agglomerated Pd nanoparticles and narrow particle size distribution dispersed on the support materials. The particle size and crystalline size of the prepared electrocatalysts were determined using HR-TEM and XRD techniques. From HR-TEM, the particle sizes are in the range of 4.685nm to 6.860nm while the crystalline sizes from XRD ranged from 3.286nm to 6.568nm. The surface areas of the supports were analyzed using Brunauer-Emmett-Teller (BET) Technique. Reduced graphene oxide (rGO) showed the highest surface area compared to other supporting materials. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to estimate the Pd metal loading for the prepared electrocatalysts and it was observed to be closest to that of Vulcan XC-72. Cyclic voltammograms showed Pd/rGO to be the most electroactive due to its higher electroactive surface areas than other catalysts. Furthermore, chronoamperometry and electrochemical impedance spectroscopy showed that catalyst supported on rGO proved to be most stable with highest kinetic rate compared to other supported catalysts examined. Hence, rGO has been proven in this study to be the best material for supporting electrocatalyst for direct methanol fuel cells.

Keywords: graphene oxide, reduced graphene oxide, n-doped graphene oxide, reduced n-doped graphene oxide, palladium catalyst, methanol oxidation, direct methanol fuel cell.

A Flexible Approach to Parameter Estimation of Physics-Based Battery Models with Bayesian Optimization

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A wealth of measurement techniques are available for determining transport or thermodynamic properties of batteries. Some examples are GITT [1], pulse experiments [2] or least squares with impedance spectroscopy [3], which are excellent at automatically retrieving a subset of model parameters with relatively low computational cost. They achieve this at the cost of accuracy and compatibility, since each employs a different approximation in order to obtain analytic expressions.

So it remains a challenge to study the interactions and effects of multiple model parameters at once, since various measurement techniques would need to be combined into one so-called cost functional. This cost functional is a function of the measurement data and the battery model parameters and can be used to determine the parameters that best describe the data. The automated computation for this usually leverages the derivative/gradient of the cost functional by the parameters. Beyond some degree of complexity, this gradient would become intractable or unfeasible to analytically calculate, making the computation expensive and/or numerically unstable.

We want to eliminate the need for those gradients. The goal is to enable automated material screening with flexible selection of various measurements. Our approach uses the existing specialized techniques (e.g. [1-3]) as a starting point and refines their results by performing simulations with randomized parameters and comparing them with all available measurements. This Monte Carlo approach is made computationally feasible by utilizing Bayesian Optimization for sparse sampling and preprocessing the measurements into intuitive features. The latter also enables us to use measurements that are most often fitted by hand, e.g. discharge curves. Additionally, we make use of a single particle model with electrolyte from [4] and/or PyBaMM [5] to make the simulations as efficient as possible, but any 1D+1D model can be used thanks to the sparse sampling approach.

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Corrosion resistance and bioactivity of silica-based coatings with borosilicate/copper glasses on stainless steel implants.

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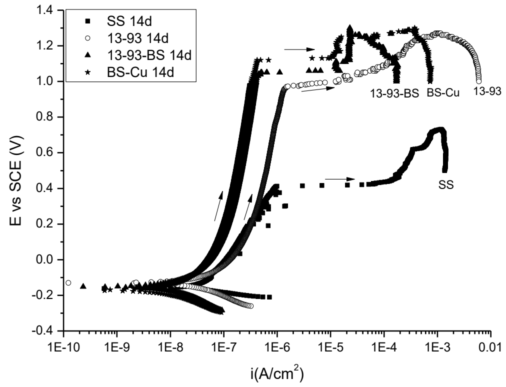
In developing countries, stainless steel is still a material that is employed for the fabrication of permanent implants as fixation plates and hip prosthesis. The aim of these implants is to replace the lost mechanical function of the damaged hard tissue, and to generate a bond with the existing bone to avoid movement and loosening. The main disadvantage of stainless steel is regarding its corrosion behaviour and the release of potentially toxic ions to the surrounding tissues when implanted [1], [2]. Besides, stainless steel does not present bioactivity and it does not exhibit any antibacterial behaviour [3]. In this context a challenge to improve the material appears: to modify the surface implant to improve the osseointegration process when cement-less implants are used to improve bone fixation and stabilization together with the searching for antibacterial properties of the material to be implanted. Since corrosion is a surface phenomenon, the implant surface and its engineering, play a key role in the performance in service of the implant.

In this work, stainless steel plane samples were coated with a hybrid organic inorganic silica based layer made by sol-gel method. The system consists in a two- layer coating of tetraethylorthosilicate, (TEOS) and methyl trimethoxysilane (MTMS). The first layer is a protective one, and the second is a functionalized one: this is achieved by the incorporation of silicate (13-93) and borosilicate (BS) glasses as a bioactive phase. Also a copper-borosilicate (BS-Cu) glass was used as an attempt of giving antibacterial properties to the surface as well as bioactivity. Surface behavior and corrosion resistance of the generated systems were analyzed by roughness measurements, adhesion of the coatings, FTIR, SEM and corrosion tests in simulate body fluid solution at 37 °C. Also antibacterial behavior was evaluated.

All coatings with the addition of silicate and borosilicate glasses showed bioactivity after 14 days of immersion in SBF. Also 13-93 glass presented the faster rate of dissolution, generating pits or holes in the coatings surface.The coatings presented a good electrochemical response, with high breaking potential and lower current density than the bare material. Although the dissolution rate of the BS-Cu and BS particles was high, the coatings presented excellent corrosion resistance.



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Influence of Cyano Substituents on the Electron Density and Catalytic Activity towards the Oxygen Reduction Reaction for Iron Phthalocyanine.

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Iron(II) 2,3,9,10,16,17,23,24-octa(cyano)phthalocyanine (OCNFePc), was tested as a catalyst for the oxygen reduction reaction (ORR) adsorbed on carbon nanotubes. The composite was analyzed spectroscopically and electrochemically characterized at pH 13 and pH 1. The composite showed close to 4 electron processes at pH 13. Computational analysis indicates that the O_2 molecule binds end-on to the metal center and that the dioxygen molecule is dissociated on both the Fe metal center and the corral ring. An Analysis of the molecular electrostatic potential confirms the behavior of cyano residues as electron-withdrawing moieties in OCNFePc. As a result of its catalytic behavior and theoretical analysis of its O_2 binding energy, OCNFePc was placed in a high position on a volcano correlation of similar phthalocyanine composites.

Effect of Thioabiraterone and Thioabiraterone-Modified Nanoparticles on Hepatocytes or Human Prostate Epithelial Cells

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Gold nanoparticles (AuNPs) conjugated with drugs are used in diagnostics and therapies [1-4]. For many years research has been carried out to form efficient drug carriers. We present novel modification of gold nanoparticles: AuNP conjugated with thioabiraterone (AuNP-S-AB) (Fig. 1). The synthesis of AuNP-S-AB and new analytical procedures are described based on the application of UV-Vis, TEM, IR, NMR and TGA. Our synthetic approach involves ligand exchange of citrates to thioabiraterone on gold nanoparticles and shows that citrate anions preadsorbed on AuNPs can be readily displaced by thioabiraterone. The biological part of the work is done on hepatocytes or human prostate epithelial cells and proved that newly synthesized thiol derivatives of abiraterone, as well as AuNP-S-AB, are more biocompatible than the original abiraterone. Biological studies have established a safe concentration of AuNP-S-AB (IC_{50}) for the vital cell functions, up to 25 μM of AuNP-S-AB can be safely used in the therapy. The idea of delivering abiraterone in the form of AuNP-S-AB is hence a promising candidate for the application in cancer therapies.

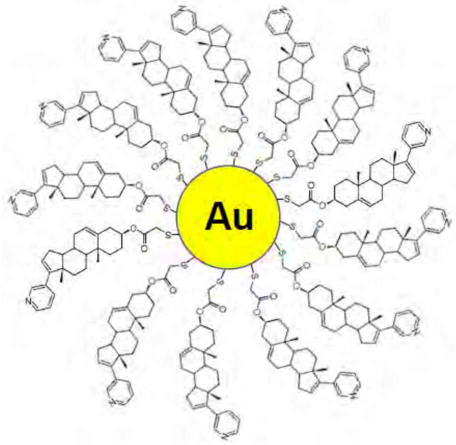

Fig. 1 Scheme of AuNP-S-AB

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Enhancing the hydrogen evolution reaction activity of platinum electrodes in alkaline media using Ni-Fe clusters

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Pt surfaces modified with non-noble metal hydroxide clusters have been examined: the Pt surfaces offer optimal hydrogen adsorption energy, whereas the non-noble metal hydroxides support water dissociation.[1] According to the Bronsted-Evans-Polanyi principle, the ability of a catalyst to dissociate water is correlated with the OH-adsorption energy. On the other hand, a too strong OH-adsorption is undoubtedly counter-productive, as the active sites get blocked. As the state-of-the-art, Pt surfaces modified with Ni-hydroxide clusters showed the best HER activity. The current understanding of the origin of such high activity is that the hydroxides facilitate water dissociation, while at the same time Pt promotes H_2 generation. Moreover, various studies on the Ni-Fe hydroxides, which are among the best catalysts for the oxygen evolution reaction (OER), proved that the addition of iron to the Ni-hydroxide films can improve their conductivity by more than 30 times.[2] It was further shown by X-ray absorption spectroscopy and coulometric titration that the addition of iron can in general increase the oxidation state of Ni atoms in the vicinity of Fe,[3] which implies an improved water dissociation ability due to the increased OH binding energy[4]. Herein, we demonstrate an easy way to improve the hydrogen evolution reaction activity of Pt electrodes in alkaline media by introducing Ni-Fe hydroxide clusters to their surfaces. As a result, the overpotential needed to achieve the current density of 10 mA cm^{-2} in 0.1 M KOH is reduced down to ~70 mV. To the best of our knowledge, these modified electrodes outperform any other reported electrocatalysts tested under similar conditions. Moreover, the influence of (i) Ni to Fe ratio, (ii) cluster coverage, and (iii) the nature of the alkali metal cations present in the electrolyte on the resulting electrocatalytic activity has been investigated. The observed catalytic performance likely originates from both the improved water dissociation at the NiFe-clusters and the subsequent optimal hydrogen adsorption and recombination at Pt atoms present at the NiFe/Pt boundary.[5]

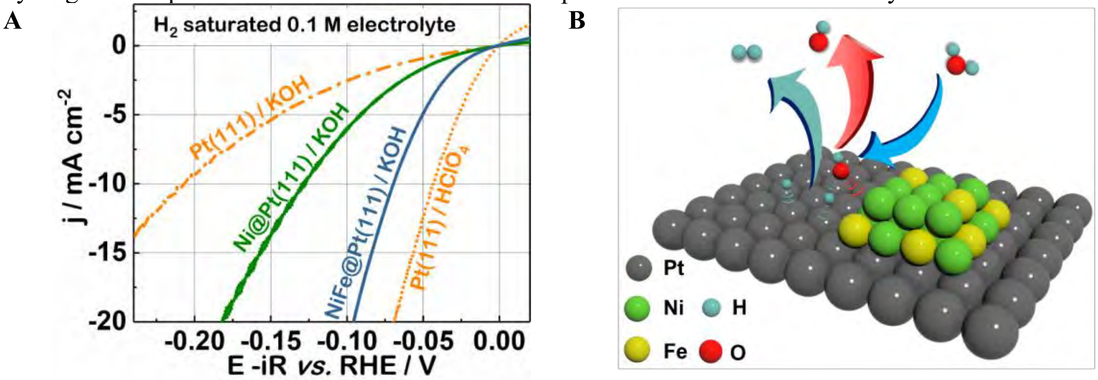

Figure. (A) Typical polarization curves of Pt(111), Ni@Pt(111), and NiFe@Pt(111) recorded in H_2 saturated 0.1 M KOH aqueous electrolytes at a scan rate of 50 mV s^{-1} and a rotational speed of 1600 rpm. (B) Proposed mechanism of HER on NiFe@Pt(111) electrodes in alkaline media.

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Tyrosine Based Electrochemical Detection of DNA

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Nucleic acids are the biompolymers which carry genetic information for protein production essential to all known forms of life. Deoxyribonucleic acids (DNA) are promising subjects for a point-of-need testing as markers of environmental contamination or human deseases. In a search for robust, portable, and sensitive DNA detection systems for *in situ* applications, the development of electrochemical sensing principles for nucleic acids is of high interest [1].

DNA are known to be electoactive through their nitrogenous bases: guanine, adenine, cytosine, and thymine [2, 3]. However, the direct electrochemistry of DNA characterizes by high oxidation/reduction potentials and low values of registered currents. Guanine possessing the lowest electrooxidation potential among nucleobases oxidizes at 0.6–0.8 V (*vs.* Ag/AgCl) [2]. Electroreduction of nucleobases takes place at the potentials over –1.5 V [3]. The signals of DNA are severely affected by the molecular weight of biopolymer [4] and the formation of double helix – nucleobases linked together by hydrogen bonds inside the DNA double helix become hardly accessible for electrode reactions [1]. To overcome this problem, we are suggesting a novel strategy for detection of double stranded DNA (dsDNA) through the tyrosine (Tyr) oxidation. As it was shown previously, there is an intercalative interaction between tyrosine and dsDNA with the binding constant of 4×10^3 mol^{-1} L [5].

In this work, oxidation of free Tyr in the presence of native DNA and Zn(II) ions was studied by square wave voltammetry on carbon screen printed electrodes. The addition of DNA to the Tyr or Tyr + Zn(II) samples induced the significant decrease of the oxidation signal at 0.6 V, especially in the presence of Zn(II) ions. The calibration curves in coordinates 'I_p (Tyr), μA – lg(c(DNA), M)' were linear from 2 to 500 μM of herring sperm DNA with different slopes in the absence and in the presents of Zn(II) ions. At the same time, direct electrochemical detection of the DNA through the oxidation of guanine residue (Gua) at the potential of about 0.8 V gave a linear calibration curve in coordinates 'I_p (Gua), μA – c(DNA), M' from 10 to 500 μM. Other amino acids tested, namely cysteine (Cys) and tryptophan (Trp), which electrochemical oxidation occurs in the same potential range as Tyr (0.5–0.7 V), demonstrated no pronounced effect of DNA on their signals both in the absence and the presence of Zn(II) ions. The oxidation signals of Cys or Trp just slightly decreased and shifted to more positive potentials in the presence of DNA. Interesting, that these amino acids demonstrated unequal responses to addition of Zn(II) ions (DNA free controls): oxidation peaks of Tyr and Trp decreased, while the signal of Cys became more developed. To detect DNA, instead of Tyr, well-known redox indicator $K_3Fe(CN)_6$ was studied as well, but found less sensitive to the presence of DNA than free Tyr. Finally, two possible mechanisms of registered decrease of Tyr oxidation peak may be suggested: (i) a formation of the complex between Tyr, DNA, and Zn(II) ions; (ii) the blockage of Tyr oxidation by the DNA adsorption on electrode surface, enhanced by Zn(II) ions.

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Deoxyuridine Triphosphates Modified with Amino Acid Side Chains for Direct Electrochemical Detection of Double-Stranded DNA

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The detection of nucleic acids – macromolecules that store genetic information and enable protein production – is of a great interest for fundamental and applied biochemical studies. Nuclec acids are promising subjects for a point-of-use testing as markers of environmental bacterial and viral contaminations or human deseases. Deoxyribonucleic acids (DNA) are known to be electoactive through their nitrogenous bases: guanine, adenine, cytosine, and thymine [1]. However, the direct electrochemistry of nucleic acids suffers from high oxidation/reduction potentials and low values of registered currents. Guanine possessing the lowest electrooxidation potential among nucleobases oxidizes at 0.6–0.8 V (*vs.* Ag/AgCl), while 2'-deoxyguanosine-5'-triphosphate (dGTP) oxidizes at 0.9–1.0 V [1]. The oxidation current is strongly affected by the length of a nucleic acid strand [2] and the formation of double helix – nucleobases linked together by hydrogen bonds inside the helix become hardly accessible for electrode reactions [1]. To overcome these problems, an exciting strategy of electrochemical sensing of nucleic acids has been suggested by M. Hocek and M. Fojta with coworkers [3]. They inserted a palette of electrochemically active moieties into nucleic acid sequences by polymerase incorporation of chemically modified nucleotides.

In this work, we present a set of 2'-deoxyuridine-5'-triphosphates (dUTP) modified with amino acid side chains attached through a linker at the C5 position of the pyrimidine ring which can be introduced into double stranded DNA (dsDNA) by polymerase chain reaction (PCR) [4, 5]. The modified nucleotides and corresponding PCR products were studied by square wave voltammetry on carbon screen printed electrodes suitable for *in situ* analysis. A strong effect of all additional functional groups on the electrochemical behavior of dUTP was revealed. Compared to the 2′-deoxythymidine-5′-triphosphate (a natural substrate for DNA polymerases), oxidation of dUTP derivatives took place at less positive potentials. In particular, 5-aminoallyl-dUTP derivatives modified with indole acetic, indole-3-propionic, indole-4-butyric, or 4-hydroxyphenylacetic acids demonstrated well-defined oxidation peaks at 0.5–0.7 V, similar to tryptophan and tyrosine amino acids, respectively. These signals were about 0.2–0.3 V less positive than the oxidation potential of dGTP. Moreover, PCR-generated dsDNA fragments (amplicons) with modified nucleotides showed novel oxidation signals at micromolar concentrations, while no peak was observed for unmodified dsDNA at the same conditions. Therefore, the tested dUTP derivatives well complement the existing collection of electroactive 'labeled' nucleotides for direct electrochemical detection of nucleic acids. The main advantage of the developed dUTP is a good compatibility of amino acid side chains with polymerase enzymes including those used in PCR.

This work was financially supported by the Russian Science Foundation, grant 19-14-00247.

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Forensic electrochemistry: A voltammetric screening method to identify selected synthetic cannabinoids

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At present, numerous synthetic cannabinoid (SC) products are emerged and available for sale online as well as off-line with a variety of street names 'spice' and K2, and in the form of herbal incense. It is extremely important to identify these SC which are described as new psychoactive substances (NPS) presented in the herbal mixtures, to control the health, regulatory and legal risk associated with the production, sale and consumption of these products.[1] These illicit drugs can result in binding cannabinoids receptors CB1, and CB2 relatively with higher empathy and effectiveness of 100 times stronger compared to natural cannabis marijuana Δ^9-tetrahydrocannabinol (Δ^9THC).[2] Forensic scientist finds it challenging to identify SC in biological and street samples. Although gas chromatography-mass spectrometry (GC-MS) is considered as a gold standard in forensic field specifically for the identification and quantification of SC. However, it is a bulky, expensive and laboratory-based instrument. In addition, these compounds do not have screening methods such as presumptive test that can be used. [3] Thus, there is a need for new portable screening tools to detect these NPS with no conventional drug screening methods available to fulfil this task and thus, require developing a necessary on-site screening tool for NPS detection that can be utilised for street and toxicological samples. Currently, electrochemical techniques have shown promising results for the detection of 5F-ADB-PINACA and STS-135 which are indazole and indole derivatives of SC. Initial results for the detection of SC are explored here. Differential pulse voltammetry (DPV) provides excellent sensitivity with limits of detection of 0.3 nM and 0.5 pM of indazole and indole-base respectively. Practical responses to the challenges such as the availability of reference standards and validation methods cannot match the increase in varieties of NPS reported by laboratories.[4] A rapid and a non-destructive analytical method is needed in forensic drug and toxicological analysis and this works highlights the promise of electrochemical sensors to address this gap.

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Feasibility of demand response in the chemical industry

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Abstract

In the field of power generation, the aim is to increase the part of renewable energy. This brings an increase in fluctuations in power supply, which leads to a higher need for adaptability, meaning more flexibility in production and consumption of electricity. Load changes in energy-intensive industries as seen in the chemical industry would be a way to provide this. In the joint project ChemEFlex the feasibility of demand response in various electrochemical processes of the chemical industry is analyzed. In this work, two processes with different levels of development were studied by evaluating suitable operating parameters and their tolerable limits. The commercialized process for the electrohydrodimerization of Acrylonitrile (ACN) to Adiponitrile (ADN) was the first case considered suitable for further studies:

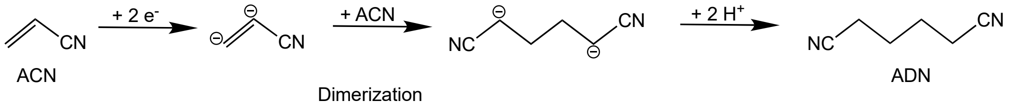

Fig. 1: Electrohydrodimerization of Acrylonitrile to Adiponitrile.

Adiponitrile is an intermediate in the production of Nylon. Worldwide the production rate of ADN is around 1,31 Mio. t/a, of which 300.000 t are made through cathodic hydrodimerization. This makes the so-called Monsanto-Process the most important electroorganical synthesis.

The second case is the piloted process of the electrohydrodimerization of Formaldehyde to Ethylene glycol.

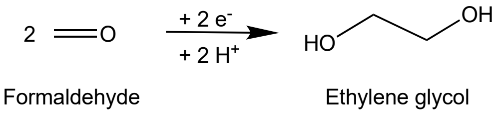

Fig. 2 : Electrohydrodimerization of Formaldehyde to Ethylene glycol.

Ethylene glycol nowadays is almost exclusively made from direct oxidation of Ethylene, followed by hydrolysis of Ethylene oxide. Even though this process has a poor selectivity and is high in energy consumption, the use of mineral oil results in a very low price. Still, with increasing prices for crude oil and the additional profit from the control energy market, the electrochemical process could be a good alternative.

Experimental section

Two experimental plants were built in a laboratory scale [1], [2] to test the application of demand-side management. The changes in selected parameters like aging of electrodes, product quality, etc. are documented and evaluated while various flexibility profiles (load changes in seconds or minutes, adapted to the requirements of the control energy market) were applied.

Experiments were carried out in Microflowcells by ElectroCell AB (Sweden). For the Monsanto-Process the effects on an undivided cell were studied, whereas for the synthesis of Ethylene glycol, a Nafion 324 membrane was used for separation.

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Treatment of Water Polluted with Cr (VI) Using an Electrodialysis System

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The metals in aqueous state are substances commonly found in water from various processes, such as electroplating and mining, among others. Some of the metals found in this kind of effluents attract attention because they have an adverse effect on the environment and on health, such as substances as chromium, cadmium, arsenic and lead, mainly; this is why the discharges with the presence of these metals are regulated through environmental standards [1]. However, it is a fact, that there is a growing need to develop better methods for the removal of metals, and thus avoid a negative impact on the environment. In the particular case of chromium, it is known that it is an element used for decorative purposes and protection against corrosion and in its trivalent form it is necessary during the human metabolism. However, this element has the peculiarity that, being in a more oxidized state, Cr (VI) has characteristics that relate it to diseases such as cancer, being that this is one of the most stable states of chromium and very much used in the processes described above, as pigments industry [2].

In this sense among the methods that exist for the elimination of metal ions is the electrodialysis, which is an electrochemical technology that allows the separation of aqueous ions, releasing the effluent of these and allowing to recover the component in question [3, 4]. Therefore, the present work addresses a study of hexavalent chromium removal, from a synthetic solution of 100 ppm of Cr (VI) using an electrodialysis small cell, with electrodes of stainless steel and titanium mesh, of 30 cm^2 of effective area, seeking to have a free effluent of the metal. The results obtained showed an energy consumption of 1.14 kWh per m^3, with a total removal of the pollutant. The above shows the potential of the technique to be used with other types of ionic contaminants and be scaled and the obtaining of valuable sub products.

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Galvanic Cell Operated with Hexavalent Chromium to Remove It

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Hexavalent chromium is considerate a toxic compound to the human health [1], this is why, find new strategies to remove it become important. Traditional methods involve the use of chemicals to achieve the precipitation of this compound, which implies filtration systems and solids waste generation [2]. In other hand, some electrochemical methods to remove it have been showing efficiency: as electrochemical filtration [3] or electrodialysis; nevertheless, although the results are promising, ever that implies the use of an external potential application, which means an extra energy cost. This is a limiting, since that it mean that the use of this technologies are exclusively in places with access to electricity.

In this work, we proposing a system that does not need external potential, conversely, the system gives it. The main goal was the removal of hexavalent chromium from a synthetic solution, but without the use of an external electric field applied. For this, we use a membrane´s electrochemical cell, where by two compartments, of 30 cm^2 of effective area, separated by ion exchange membranes, synthetic solution of potassium dichromate were recirculated at 20 mL per min, and a third compartment with hydrogen peroxide were recirculated. We add a salt in one compartment to promote a chemical reaction in the electrodes compartments and so an electrical field between them and the pH were adjusted. After 22 hours of operation, the system removed 90% of the hexavalent chromium from one channel, and at the same time, energy was generated.

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Simultaneous monitoring of the electrochemical behavior of both positive and negative carbon electrodes of electrochemical double layer capacitors in different electrolytes

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Despite their high power and high energy contents comparing to other capacitor technologies, electrochemical double layer capacitors still suffer from several drawbacks which limit their widespread use. In order to boost their performance in the applications where batteries are currently used, the electrical and electrochemical properties, such as energy content, ohmic resistance and self-discharge rate, need to be improved.

The testing of supercapacitors is routinely done by electrochemical methods in two-electrode system. With such methods overall properties of supercapacitors are obtained. However, in order to make further improvements of supercapacitors properties, it is of key importance to separate the processes occurring at both electrodes during charging/discharging reactions. Such measurements would reveal electrodes of limiting capacitance, potential distribution through the supercapacitor as well as the occurrence of various resistances within different parts of the cell. The aim of this work was to simultaneously test the electrochemical properties of both electrodes of self-assembled supercapacitors in different electrolytes by inserting a Pt wire as a reference electrode inside the separator.

Supercapacitor carbon electrodes consisting of activated carbon (AC), carbon black (CB), and poly (vinylidene fluoride) (PVDF) as a binder, were made in the lab by mixing the aforementioned ingredients in the ratio of 80:10:10. The dry mixture were then dissolved in N-mehtyl pyrrolidone (NMP) to form a paste which were painted at to an aluminum current collector in the form of a thin film. After drying the film was cut into circular electrodes. The electrodes were then used in the construction of a supercapacitor with different electrolytes consisting of different tetraalkylammounium and lithium salts in an EL-CELL three electrode cell. The supercapacitor had a layered structure consisting of two electrodes on each side of a fiberglass separator. The reference electrode was Pt foil aligned to the side of the separator so that it was in contact with it but did not interfere with the charge flow between the electrodes.

Both DC and AC techniques have been used to determine the behavior and status of each electrode during the operation of the supercapacitor. Firstly, a large number of charge/discharge cycles were performed with “staircase” impedance measurements at regular charge/discharge intervals. The aim was to observe the changes of potential and the impedance response on each electrode during the initial “conditioning” of the supercapacitor. Secondly, the charge redistribution was monitored on each individual electrode by letting the supercapacitor rest when fully charged and also by keeping either electrode at a constant potential while observing the potential changes of the other electrode.

Significant differences between the responses of positive and negative electrodes of the supercapacitor were noticed, primarily in the discrepancy between the potential ranges of both electrodes during cycling in each electrolyte. Also it was observed that the negative electrode possesses higher resistance values in the impedance measurements.

Mathematical Modeling of Temperature Dependent Degradation of Supported Pt-based Electrocatalyst in Voltage Cycling Experiment

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Hydrogen fuel cells, employing carbon-supported platinum-based materials to catalyze oxygen reduction reaction, represent one of the most promising technologies of future energy conversion. However, their wider adoption is currently limited due to the relatively fast degradation of the membrane electrode assembly during their operation, decreasing their performance and limiting their life-time.

To improve the understanding of degradation phenomena in the fuel cell catalyst, recently developed mechanistic model [1] of platinum particle degradation was used to describe the decrease in electrochemical surface area (ECSA) during accelerated stress tests on supported platinum based electrocatalysts in thin film rotating disc electrode setup. The model describes several degradation processes by mathematically modeling the rates of electrochemical phenomena, i.e. platinum and carbon surface oxidation and corrosion, which strongly depend on the local electric potential and temperature according to Arrhenius law. The dissolution of platinum from smaller particles and its redeposition on larger particles, the so-called Ostwald ripening, leads to the net growth of platinum particles and consequent decrease of ECSA [2], while the corrosion of carbon support results in detachment of particles and their eventual agglomeration into larger clusters, again causing the loss of ECSA. Both of these phenomena are described by mathematical modeling of platinum particle size redistribution resulting from aforementioned electrochemical processes.

The model is calibrated based on the changes in ECSA of Pt/C catalyst from Tanaka Kikinzoku Kogyo (TEC10E50E) with 46.3 wt% of Pt on high surface area carbon during long-term accelerated stress test. Changes in ECSA were measured by cycling voltammetry several times during aging at various temperatures (RT, 40, 50 and 60 °C) and using two different potential windows (0.4 - 1.2 V and 0.8 - 1.2 V) for voltage cycling [3]. As shown in Figure 1, the model is capable of describing the change of ECSA for all six experiments using the same set calibration parameters, proving its merit in mechanistically describing all relevant processes of catalyst degradation. The results indicate strong effect of temperature on the rate of degradation. According to the model, low ECSA loss, detected at voltage cycling at high potential window (0.8 - 1.2 V) is attributed to the high coverage of platinum surface with oxides, reducing the rate of Ostwald ripening, and lower rate of carbon corrosion, emerging from complex dynamic interplay between surface oxide groups on platinum and carbon surface.

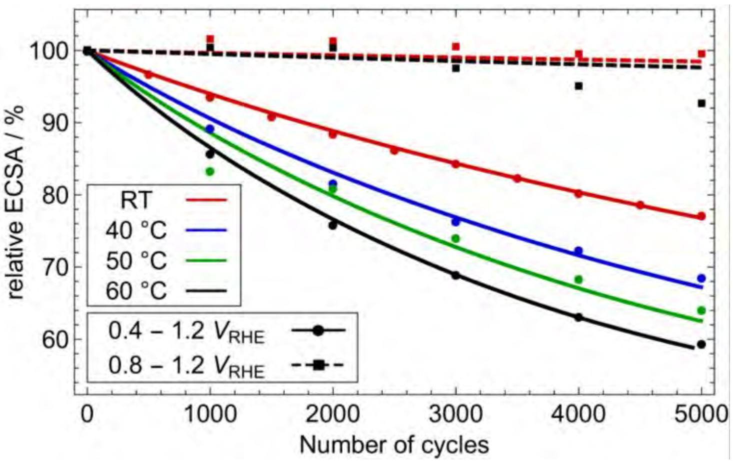

Figure 1: Comparison between measured (points) and modelled (lines) change in ECSA during voltage cycling experiment at different potential windows and temperatures.

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Gouy-Chapman versus Reality:
An Interpretation of Diffuse Capacitances using Mean-Field Methods

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The capacitance of the electric double layer is often described via the Gouy-Chapman-Stern equation as that of two capacitances in series $1/C_s=1/C_H+1/C_{GC}$, where C_H is expected to be independent of ion concentration and C_{GC} can easily be derived from thermodynamic principles for non-interacting point like particles. For concentrated electrolytes, deviations from this theory are expected and have been shown. Dilute electrolytes, on the other hand, are generally expected to follow this Gouy-Chapman-Stern behavior. In recent experiments, however, Ojha, Koper et al. [Angew. Chem. Int. Ed. 2020, 59, 711] have shown that a deviation from the Gouy-Chapman behavior can also be observed in dilute electrolytes.

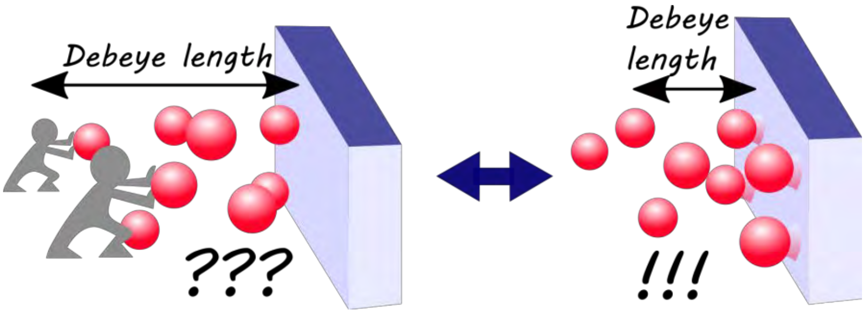

Figure 1: Experimentally, shorter screening lengths than expected are observed on Pt and Au. Our mean-field model can explain this somewhat unexpected behavior by ion adsorption.

While the ideal behavior is observed for Hg and while for all metal electrodes studied the screening length is suggested to scale with 1/√c, the inverse root of the ion density, as predicted by the Gouy-Chapman theory, the overall magnitude of the screening length seems to be considerably reduced on gold and platinum (i.e., $C_{diffuse}=\alpha C_{GC}$).

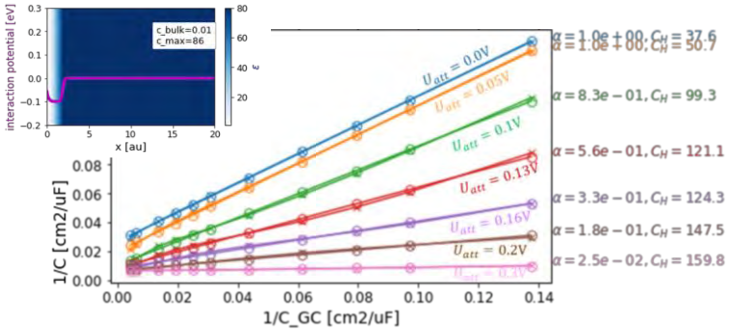

Figure 2: Results of mean field simulations for different ion adsorption strengths (crosses); circles: fit to $1/C_H+1/(\alpha\ C_{GC})$. A value of α smaller than 1 suggests a reduced effective screening length. The inset schematically shows the model used in a generalized Poisson-Boltzmann approach.

We show that such an increased screening length can be captured in mean-field theories when taking ion adsorption close to the interface into account. Extremely simple, analytical models can be used to capture this effect in idealized situations, but would lead to a non-linear scaling of the screening length with 1/√c in contradiction to experiment. Using a mean-field, modified Poisson-Boltzmann description, however, we can qualitatively reproduce the experimental data, giving a tentative interpretation to the experimental observations. Interestingly, we only observe a behavior similar to that found experimentally if ions can adsorb in regions of strongly reduced dielectric constant as shown schematically in the inset of Fig. 2, thus providing additional information on the atomic-scale behavior of the interface.

New Strategies for the Evaluation of the Anti-tumor Effect of Some Drugs using Electrochemical Techniques

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Doxorubicin is an antitumor drug from the group of anthracyclines widely used in the treatment of various malignancies like breast and bladder cancer, Kaposi sarcoma, Hodgkin and non-Hodgkin lymphoma, acute lymphoblastic and acute myeloid leukemia. It can be found on the market in different formulations, starting from lyophilized powder for injection to liposomal doxorubicin and other types of delivery systems in which it can be incorporated alone or in combination with other molecules (1).

Simvastatin is an inhibitor of HMG-CoA reductase, the most important enzyme from the process of cholesterol biosynthesis. It is use in the treatment of hypercholesterolemia to reduce serum levels of cholesterol and therefore to reduce the risk of cardiovascular diseases. There are several studies in the literature which demonstrated the decrease of cellular proliferation in the presence of high dose simvastatin and that this molecule potentiates the cytotoxic activity of antitumor drugs. Therefore, various types of drug delivery systems containing both antitumor drug and statin started to be investigated for the improvement of cancer therapy (2).

The aim of this study was to develop a disposable, simple, fast and sensitive sensor for the simultaneous electrochemical detection of doxorubicin and simvastatin, which could be used in preclinical studies of the development of a new pharmaceutical formulation for drug delivery. Firstly, the electrochemical behavior of each molecule was analyzed regarding the influence of electrode material, electrolyte solution and scan rate. After this, the proper electrode material, electrolyte solution and scan rate for both medicines were chosen and a LSV (Linear Sweep Voltammetry) procedure was optimized for the simultaneous detection. In the same time, two chronoamperometry procedures were tested, one for the detection of doxorubicin in the presence of simvastatin, and the other one for the detection of doxorubicin and simvastatin together. Finally, calibration curves for doxorubicin and simvastatin in the presence of each other were obtained using both electrochemical methods and the results obtained were compared.

This detection strategy represent a promising tool in the development of a new pharmaceutical formulation for targeted drug delivery containing both drugs, whose association was proved to bring benefits in the treatment of cancer.

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State of Health Identification of Lithium-ion Battery by Advanced Instantaneous EIS

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Electrochemical impedance spectroscopy (EIS) is the most popular non-destructive method for lithium ion batteries (LIBs) diagnosis and materials characterization. Generally, EIS is operated on a non-operational steady state of the battery system in order to satisfy the basic principles of EIS measurements, i.e., causality, linearity and stationarity [1]. In this work, EIS characterizations of LIB systems in a non-steady state or an operando condition are explored by using the in-house developed multisine technique (including both hardware and software): Odd Random Phase EIS (ORP-EIS) [2] with the time-resolved instantaneous impedance calculation [3]. This approach provides mechanistic insights into the dynamic interfacial properties of LIB systems and, therefore, can be applied for the online monitoring of battery conditions. Moreover, the in-house designed hardware is potentiostat-free setup, which shows potential to be integrated in battery management system (BMS).

This work is based on the state-of-the-art $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode material, and ORP-EIS experiments are operated in the galvanostatic mode. In the non-steady state experiment, the ORP-EIS is measured directly after charging or discharging pulses. The time-resolved impedance spectra during the relaxation period can be calculated as shown in Figure 1. The charge-transfer resistance (R_{ct}), the dominant impedance response in the low frequency region (< 10 Hz), changes with the relaxation time. The phenomena can be correlated to the alternation of ionic concentration in the interfacial vicinity. Cycling aged NCA electrode materials are measured with the identical approach. A more significant evolution of the R_{ct} during the same period of relaxation time is observed, indicating a deteriorated interfacial microstructure of NCA electrodes. This ΔR_{ct} could work as a stand-alone SoH identification parameter, which is dependent only on the interfacial condition of electrode materials.

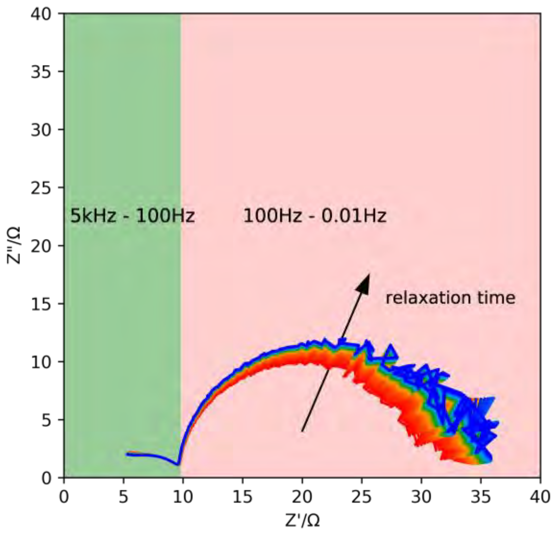

Fig.1. Nyquist plot of the time-resolved instantaneous impedance of an NCA/lithium cell during the relaxation period after the charging pulse.

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Self-powered Single-use Glucometer – A New Approach for Sustainable Analyte Detection

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Paper-based electrochemical biosensors are able to provide diagnostics and immediate health information near the patient [1]. Ideally, these point of care devices could be used by the patient with no need for laboratory instruments or trained specialists, allowing patients to self-diagnose and self-care monitoring from their own homes, enhancing their quality of life and decongesting the overloaded healthcare system. However, these devices generally require external power sources or expensive readout units [2, 3]. A new paradigm of autonomous, sustainable and cost effective, single use electrochemical biosensors is needed. One of the main difficulties in the fabrication of an autonomous sensor is the development of transducers to effectively convert the electrochemical response to a user recognizable signal without using complex electronics or sophisticated equipment.

In this work, a cost-effective, fully printable, stand-alone glucose-sensing system has been developed with an enzymatic fuel cell as the only power source and with no need for an external readout unit. A novel and simple approach to transduce the electrochemical signal from an enzymatic fuel cell into a digitalized response. A self-powered single use device for the diagnosis of gestational diabetes mellitus has been designed, fabricated and tested. The self-powered device consists of: i) an enzymatic fuel cell, which acts as both the glucose sensor and the energy source; ii) an electronic circuit, which transduces the biological response into an electrical response and ultimately into electrochromic displays that show the result; iii) and an electro-fluidic timer, which times the sequence of events and allow the connection of the different parts of the electronic circuit at specific times. The working principle of this electrochemical sensing device is based on the fuel cell response, while charging a capacitor. By monitoring the capacitor built-up voltage, the concentration of glucose can be determined. The device was able to determine whether the concentration of glucose in a sample was within healthy levels (< 140 mg/dl, 7.8 mmol/l), indicates pre-diabetes (≥ 7.8 mmol/l and < 11.1 mmol/l) or provisional diagnosis of diabetes (≥ 11.1 mmol/l) [4]. The results show reproducibility and selectivity, turning on the displays according to the glucose concentration.

This self-powered, autonomous glucose bio-sensing device offers an energy saving, environmentally friendly and low cost solution for the point-of-care testing systems. This approach is a conceptual pathway that can lead to instrument-free electrochemical biosensor design. It could potentially be used for the diagnosis of human diseases besides diabetes, by measuring concentrations of other health care parameters such as lactate, urea, ammonia, creatinine, cholesterol and uric acid. This measuring approach could dramatically contribute to the early detection and palliation of life threaten diseases in developed and developing world, in remote areas and emergency situations, since it does not need trained specialist, laboratory infrastructure or external power source.

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Influence of carbon support modification on non-noble MNC catalyst for oxygen reduction reaction

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Metal nitrogen carbon catalysts (MNC) are a promising alternative for platinum based catalysts in the oxygen reduction reaction (ORR) in PEM fuel cells, but at the moment state of the art MNC catalyst still suffer from low activity and instability. Wang *et al.* showed the positive effect on catalyst activity, by using carbon supports as basis to depose and polymerize the precursors.[1] In this work we studied interactions of surface functionalization on the polymer deposition and their characterizations in regards to their activity.

The surface of two commercial carbon supports, Ketjenblack EC-600JD and MWCNT were functionalized by two methods: oxidizing and grafting of functionalized benzenes. Functionalities such as sulfonic acid and nitrate groups were achieved by radical grafting via *in situ* formed diazonium compounds. The modified carbon supports were characterized by infrared spectroscopy, XPS as well as elemental analysis.

The functionalized carbons were used as support for later oxidative polymerization with different nitrogen containing monomers: *m*-phenylenediamine, *p*-phenylenediamine, aniline and melamine. In order to obtain the final catalyst, the support/monomer mixes were polymerized, impregnated with iron precursor, pyrolyzed at 950 °C and acid leached of unspecifically bound iron species.

The final catalysts were characterized for their electrochemical activity in rotating ring disc setup, their site density via CO-chemisorption and their respective turnover frequency. The physicochemical characterization consists of the analysis of surface area and pore structure via nitrogen physisorption, SEM and TEM; for the surface structure and compositional analysis via elemental analysis, ICP-OES, and XPS.

We could show improved mass activities up to 0.95 A g^{-1} at 0.85 V_{RHE} with surface modification of the used carbon supports in comparison to the unmodified carbon supports or no carbon support. The good dispersion of nitrogen containing monomers is assumed to lead to increased surface area and high site density. Applying this highly scalable method of surface functionalization to different synthesis methods for MNC catalysts could be a viable way to achieve high performance catalysts for ORR.

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Dramatic Differences in the Electrochemical and Spectral Behavior of Hexameric and Heptameric DNA Fragments

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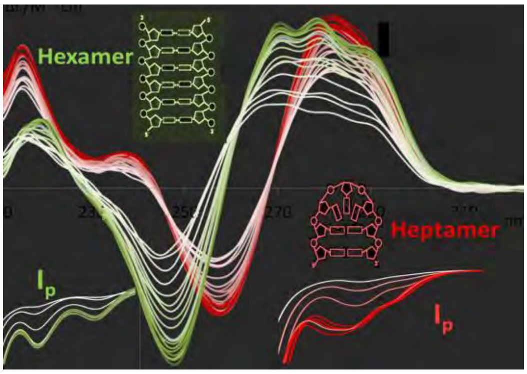
Dramatic electrochemical and spectroscopic differences, caused by the loss of the adenine nucleotide residing in the middle of the heptamer d(GCGAAGC), were revealed [1]. Based on comparative voltammetric, circular dichroic and electrophoretic studies of the hexamer (Hx) - d(GCGAGC) and the heptamer (Hp) - d(GCGAAGC) we illustrate how a single nucleotide sequence and a neighbouring nucleotide species in ODNs strongly affect their secondary structure.



Dedicated studies suggest that the heptamer (Hp) possesses a hairpin structure, whereas the hexamer (Hx) appears to be rather a duplex. Both of the structures exhibited completely different adsorption behavior at the hanging mercury drop electrode, and this factor was readily confirmed by means of elimination voltammetry with linear scan (EVLS) [2]. We established that the Hp hairpin (~ -1300 mV), compared to the Hx duplex (~ -1360 mV), is the thermodynamically favored electron acceptor. The adsorption isotherms were constructed based on the voltammetric peak height values, reflecting the reduction of the adenine (A) and cytosine (C) moieties as well as the oxidation of the 7,8-dihydroguanine (7,8-DHG) moieties [3,4]. The comparative spectroscopic and electrochemical studies of heptameric and hexameric DNA fragments showed that not only the Hx structure but also the Hp structure (denoted as a thermodynamically very stable formation in solutions [5]) is vulnerable by an electrode field.
Finally, as revealed by both the spectroscopic and electrochemical results, Hx forms a bimolecular antiparallel homo-duplex carrying both Watson–Crick base pairs (CG or GC) and mismatched edge-to-edge base pairs (GA or AG).

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Ara h1 Food Allergen Electrochemical Detection by Gold-Chip DNA-based Sensor

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In 2015, World Health Organization (WHO) published a detailed report of an estimation of the global burden of foodborne diseases. According to this, there are four leading causes of unsafe food due to the presence of viruses, harmful bacteria, parasites or chemicals [1]. The latter is further categorised into aflatoxins, arsenic, cassava cyanide, peanut allergens and dioxins. Food allergy affects 1-10 % of the population and reports show that its prevalence in children increased by 50% between 1997 and 2011 [2]. Peanuts are one of the most common allergic reaction-induced foodstuffs as being often introduced in human dietary. The most frequently allergenic protein which is responsible of peanuts allergy is Ara h1, 2, 3, and 6 triggering to an immunological response in more than 50% of the allergic population representing the first leading cause of anaphylactic fatalities worldwide [3]. Symptoms can occur from minutes to hours after exposure, and may include difficulty in breathing, low blood pressure, itchy rash, swelling of the tongue, and life-threatening systemic reaction called anaphylaxis. As there is no cure for peanuts allergy yet developed but only effective care and emergency treatments, the only viable solution is a free peanut-based diet. ELISA is the most commonly used method for determining low levels of food allergens in food (ingredients, processed foods and beverages) [4], but lacks of simplicity and reduced costs and oftentimes leads to delays in acquiring results. Therefore, risk management and mandatory labelling system of food allergens are critical steps in food industry to guarantee consumers safety. For these reasons, the development of an easy-to-use, fast and accurate device for peanuts allergen detection is fundamental to prevent life-threatening reactions in sensitized subjects.

This work presents the electrochemical detection of Ara h1 by means of a biomimetic approach using oligonucleotide-modified microarray gold chips. The sensing strategy for the production of DNA microarrays was performed using a 32-electrode chip comprising of (70 × 70 μm^2) gold electrodes [5] and synthetic DNA strands with sequences specific to Ara h1. The affinity reaction was performed on microarrays consisting of 32 individually addressable modified gold microelectrodes. The affinity reaction between the DNA strands and Ara h1, followed by conformational and structural changes in the recognition layer, was triggered by means of electrochemical mediators labelled at the DNA sequence. Each step of electrode modification was characterized by electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy, and chronocoulometry for determination of DNA coverage. Possible applications on food sample analyses will be presented.

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Quantum-Chemical Modeling of Structure Modification in Neutral Polypyrrole Complexes with Anions

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Polypyrrole is widely used in various electronic, electrochemical, and membrane technologies as an electroactive polymer with high electrical conductivity and high chemical stability [1]. For the vast majority of polypyrrole applications in various electrochemical devices is the fundamentally important question of the range of electroactivity potentials and conductivity of the polypyrrole chain, a change in these parameters during redox transitions from a charged to an uncharged state, as well as concomitant changes in other polymer parameters.

Recently, an interesting experimental effect for thin films of polypyrrole noticed by authors of work [2]: the electroactivity region expands into the negative potential region when such films undergo multiple charge/discharge cycling in a monomer-free solution of the background electrolyte. In this case, the questions arise - does the expansion of the electroactivity potentials range correlate with a conductivity change of the material during multiple cycling of thin polypyrrole films, and what is the reason for this correlation? It was found that at the first stage of this process, the characteristics of the system (redox charges, shape of voltammetric response) noticeably change, and then reach saturation, which can be caused by structural changes in the polymer. This work aims to find out whether the conformational changes of macromolecular complexes with anions can cause the observed behavior.

We considered the change in the shape of the polypyrrole chain upon interaction with strong acceptors (for example, BF4–) and during the formation of neutral oligopyrrole complexes with a different number of anions. The quantum chemical modeling was performed using the density functional B3LYP and basis 6-31G*. It has been shown that in such complexes, it is energetically favorable to reorient the pyrrole rings closest to the anion from the trans to cis position, which leads to the formation of meanders, including 3–5 pyrrole rings per loop. It was noted that a decrease in the loop size would decrease the interaction energy with the acceptor. Contrary, an elongation of such a loop reduces the number of attached anions with a slight energy change of interaction of each of them with the polypyrrole chain.

The vibrational spectra of oligopyrrole complexes with a different number of BF_4^- anions were calculated, and the prospects for the experimental detection of calculated conformational states by IR spectroscopy were evaluated.

Acknowledgments

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Colorimetric Sensing System Based on Multiplexed Enzyme Assay Mediated by Smartphone Camera Readout

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Polyaniline (PANI) is a conducting polymer highly sensitive to pH changes in its microenvironment and its conductivity is known to increase by 8–10 orders of magnitude on doping with acids. This is due to the transition of its emeraldine salt (ES) form to emeraldine base (EB) which is also accompanied by colour change from green to blue [1].

In this work, we present a smartphone-based naked eye one spot biosensor utilizing the unique colorimetric properties of the poly(aniline-co-anthranilic acid) (ANI-co-AA) composite film coupled with tyrosinase (Tyr), horseradish peroxidase (HRP) and bi-enzymatic horseradish peroxidase-glucose oxidase (HRP-GOx). The enzyme is immobilized on the composite polymer film by physical adsorption and in the presence of its substrate, catalyzes a reversible redox color change in the host polymer from green to blue (Fig. 1). A Google Play Store, free of charge software application, was used to enable easy and clear display of the sensors' response indicating remarkable changes in the optical features. Transmission Electron Microscopy (TEM) and Attenuated Total Reflectance-Infrared Spectroscopy (ATR-IR) were used for the characterization of synthesized composite. The poly(ANI-co-AA) enzyme-modified films were applied to colorimetric detection of catechol, hydrogen peroxide and glucose, respectively. The developed colorimetric biosensor was studied and optimized in relation to different experimental parameters by using a 96 micro-well plate plastic support and different polyester strips were imagined. A linear correlation between the analytes concentration (0-200 μM) and the Hue value of the colored modified film was observed after only 2 minutes reaction in the case of Tyr- and HRP-based sensor, and 8 minutes for HRP-GOx sensor. The results were confirmed by the spectrophotometric measurements performed at 655 nm. By smartphone camera readout and analysis, LODs of 12.31 μM, 51.20 μM and 49.42 μM were obtained for catechol, hydrogen peroxide, and glucose, respectively. Different molecules with similar structure were tested as interferences for glucose determination. Moreover, the sensor being disposable, its applicability to food and pharmaceutical analysis was demonstrated. It has been shown by these studies that the naked eye biosensor is promising as quick and simple test for handheld analysis in various fields [2].

Fig. 1. Colour change of the Tyr/poly(ANI-co-AA) sensor in the presence of catechol in 0.1 M PB pH 5.0

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CoO_x Nanoislands on Au(111) – Structure, Stability, and Dynamics under Reaction Conditions

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Cobalt oxide is a highly active electrocatalyst for the oxygen evolution reaction (OER)[1] and a model system in electrocatalysis.[2, 3] In order to study the stability and dynamics of cobalt oxide we investigated well defined CoO_x nanoislands on Au(111) by complimentary electrochemical in-situ methods and surface science techniques. We prepared the CoO_x nanoislands by physical vapor deposition (PVD) in ultra-high vacuum (UHV) using a procedure described previously.[1] We characterized the system in UHV by scanning tunneling microscopy (STM). After transferring the sample from UHV into the electrochemical environment, we studied the system by electrochemical STM (EC-STM), on-line inductively coupled plasma mass spectrometry (ICP-MS), and cyclic voltammetry (CV). The studies were performed at pH 10 (phosphate buffer) in a potential region from -0.4 to 1.8 V_{RHE}.

After preparation, we observed two types of nanoislands, which we assign to bilayers and double bilayers. At 0.7 V_{RHE} the nanoislands are stable and do not show mobility. By decreasing the potential to 0.5 V_{RHE}, we observe that the bilayers become dynamic and start to dissolve. Online ICP-MS measurements show that Co dissolution is highest for potential steps from 0.8 to 0.5 V_{RHE}, while the dissolution rate decreases by stepping from 0.8 V_{RHE} to lower potentials. This indicates that the dissolution process is transient. Close to the reduction potential of Co^{2+} to Co^0, we observe the redeposition of (adsorbate covered) Co aggregates on the Au surface.

Scanning from 0.8 V_{RHE} in the positive scan direction bilayers and double bilayers are stable up to a potential of 1.0 V_{RHE}. At 1.1 V_{RHE} striped features appear on the bilayers which we assign to oxygen adatoms. These oxygen adatoms fully cover the bilayers upon increasing the potential further. At 1.5 V_{RHE} we observe oxidation of the Au(111) support.

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Secondary Alcohols as Rechargeable Electrofuels: Electrooxidation of 2-Propanol at Pt and PtRu electrodes

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Isopropanol (IPA) and its dehydrogenated counterpart acetone (ACE) can be used as a rechargeable electrofuel. In this concept IPA is oxidized to ACE in a fuel cell and, subsequently, hydrogenated again catalytically.[1]

Addressing this concept, we investigated the IPA oxidation on catalysts with different levels of complexity, ranging from single crystal surfaces to commercial alloy catalysts. Specifically, we used Pt single crystals as well as polycrystalline and nanostructured Pt electrodes.[2] Further we studied carbon supported Pt and PtRu model electrocatalysts, which we prepared in ultra-high vacuum,[3] as well as commercial Pt and PtRu electrocatalysts.[1]

We investigated the reaction mechanism of the isopropanol oxidation as well as the catalyst stability using complimentary in-situ techniques. Namely, we used electrochemical infrared reflection absorption spectroscopy (EC-IRRAS), cyclic voltammetry (CV), differential electrochemical mass spectrometry (DEMS), electrochemical real-time mass spectrometry (EC-RTMS), electrochemical scanning tunneling microscopy (EC-STM), and online inductively coupled plasma mass spectrometry (ICP-MS).

We observe the onset for the IPA oxidation on Pt electrodes at 0.3 V_{RHE}, yielding ACE formed with high selectivity. At potentials above 0.9 V_{RHE}, the formation of Pt oxide inhibits the reaction. The only side reaction observed is the formation of small amounts of CO_2. We show that the product ACE adsorbs at the Pt electrodes poisoning the surface. On nanotubular electrodes with high surface area, ACE stays mainly adsorbed on the surface and only a small fraction desorbs. These observations suggest that poisoning of the Pt electrode by adsorbed ACE limits the oxidation of IPA. However, we did not observe any influence of the IPA oxidation on the stability of the electrocatalysts. By using PtRu alloy catalysts, the onset potential is shifted down to 0.1 V_{RHE} and the poisoning can be reduced.

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Electroreduction of Ni and Co in the presence of MWCNT in choline chloride based ionic liquids

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Choline chloride-ethylene glycol (1:2) ionic liquid (ILEG) has been used as electrolyte to study nickel-cobalt alloy electrodeposition process and the influence of multi wall carbon nanotube (MWCNT) presence on NiCo MWCNT composite deposition processes.

Cyclic voltammograms were recorded at different scan rates in the range 10-200 mV s^{-1} on platinum electrode in Choline chloride-ethylene glycol (1:2) electrolyte containing 0.5 M Ni^{2+} and 0.5 M Co^{2+} ions. The cyclic voltammograms illustrated that nickel-cobalt and nickel-cobalt MWCNT reactions involve quasireversible processes. The experiments were recorded at a constant temperature of 70^0C.

The electrochemical cell contained a Pt electrode as working electrode, a Pt plate as auxiliary electrode, and an Ag wire immersed in the ionic liquid as quasi-reference electrode.

In order to demonstrate the mass-transport control (diffusion control) of cathodic process, we represented the plots of cathodic peak current (I_p) *versus* the square root of scan rate ($v^{1/2}$). (Fig. 1)

The deposits surface shows a rather rough surface with irregular cone deposits that increase with increasing current density. In the case of composite films, the carbon nanotubes incorporated in the film can be observed.

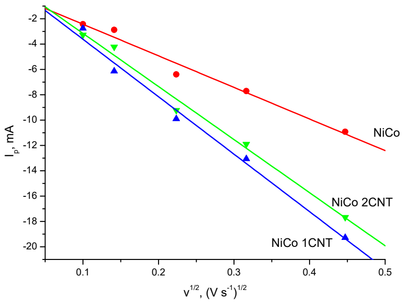

Fig. 1 The current densities of cathodic peaks *versus* scan rate for NiCo and NiCo MWCNT deposition in ILEG

The presence of MWCNT leads to an increase of the current density and an increase of the diffusion coefficient from 0.56 $\times 10^{-7}$ cm^2 s^{-1} for NiCo alloy to 1.85×10^{-7} cm^2 s^{-1} for NiCo MWCNT composite.

The obtained results of diffusion coefficients are at the same order of magnitude as calculated for Ni by Urcezino et al [1] and Co by Cojocaru et al [2].

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Deep Eutectic Solvents Based on Lithium Nitrate and Acetamide as Electrolyte in High-Temperature Electric Double-Layer Capacitors

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Electric double-layer capacitors (EDLCs), have received much attention in recent years because of their outstanding properties such as long cycle life (cyclability) and high power density sustained. Currently, the most commonly used electrolytes in EDLCs are aqueous solutions, as far as the sustainability is concerned. However, solvent evaporation and components corrosion are major drawbacks at elevated temperatures, e.g. 100°C. Organic solvents, because of their flammability and environmental toxicity, could be also discarded for high-temperatures applications. Ionic liquids may be another solution, but their production price is too high for commercial use yet. Therefore, a promising solution for high-temperature operating capacitors is the use of electrolytic solutions based on deep eutectic solvents (DESs). These electrolytes can be easily obtained just by mixing two compounds in specific molar ratios. Usually, DES are thermally and electrochemically stable and have negligible vapour pressure. Furthermore, by using high temperatures, one can eliminate several problems related to the viscosity of liquids, and thus even improve the conductivity or ionic mobility.

In this work, the properties of DES made of lithium nitrate and acetamide as the electrolyte for high-temperature capacitors were examined. A mixture of acetamide and $LiNO_3$ in the molar ratio of 78:22 is observed to form a DES with freezing point below room temperature. Basic electrochemical tests were carried out, such as cyclic voltammetry, galvanostatic charge/discharge and impedance spectroscopy; the capacitance values obtained for symmetric capacitors with porous carbon electrodes was ca. 133 $F \cdot g^{-1}$ at mild current regimes. In further studies, optimal capacitor operating conditions were determined, i.e. voltage - 1.4 V and current density - 0.2 $A \cdot g^{-1}$. Under these conditions, it has been shown that the DES mixture has better capacitance than individual components separately. The addition of organic solvents or water reduces the quality of the electrolyte at 100°C. Lithium nitrate and acetamide mixture was compared with 5M $LiNO_3$ aqueous solution as electrolytes in EDLCs and proved the advantage of DES over aqueous solutions at elevated temperatures. The processes occurring on both electrodes were also explained. Furthermore, it has been shown that changing the Li^+ cation to K^+ or Na^+ does not significantly affect the quality of the capacitor, while the change of the NO_3^- anion to NO_2^- causes a significant deterioration of capacitance properties. The cycle life of the capacitor and the effect of the addition of inorganic salt on conductivity were also investigated. The tests were carried out on various electrode materials, however, microporous Kynol ACC-507-20 turned out to be the most suitable one. Moreover, detailed analysis has been conducted using gas chromatography, DSC, Raman and FTIR spectroscopy.

The European Research Council is acknowledged for the financial support within the Starting Grant project (GA 759603) under European Unions' Horizon 2020 Research and Innovation Programme.

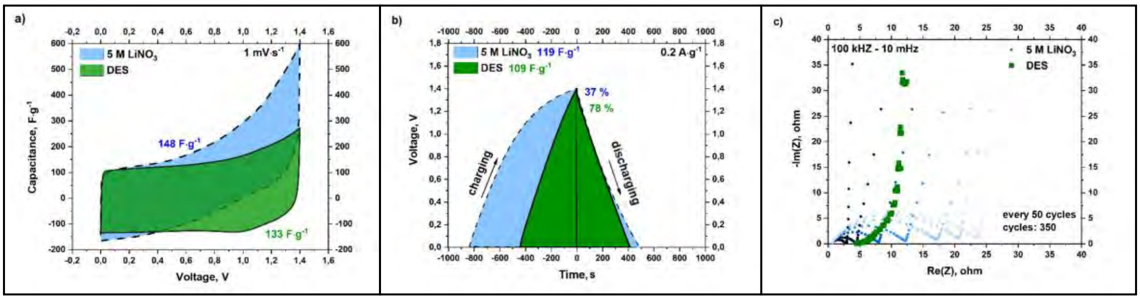

Figure 1: a) cyclic voltammograms ($v = 1\ mV \cdot s^{-1}$, $I = 0.2\ A \cdot g^{-1}$) with current values recalculated prior to scan rate; b) galvanostatic charge/discharge ($I = 0.2\ A \cdot g^{-1}$); c) Nyquist plot (100 kHz – 10 mHz) in first 350 cycles of EDLCs based on 5M $LiNO_3$ and DES at 100°C.

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Impact of nitrates ions on the corrosion mechanisms of a silicon-rich stainless steel in nitric acid media at boiling temperature

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The reprocessing process of spent fuel is carried out in France using the Purex process. The first chemical step of this process is the dissolution of the spent fuel in aqueous concentrated and hot nitric acid. Corrosion is an electrochemical process involving oxidation and reduction reactions in which the anodic reaction is influenced by material factors, whereas the cathodic reaction is influenced by environmental factors. Corrosion of stainless steels in nitric acid is strongly affected by the cathodic reaction. [1-2]

The silicon-rich stainless steel X1 Cr Ni Si 18-15-4 evaluated in this study, spontaneously forms a protective oxides film that is composed of mixed chromium and silicon oxides. This film ensures good durability of the industrial facilities operating with hot and concentrated nitric acid in the presence of oxidizing species. In particular, it has been shown that this alloy is not subject to transpassive intergranular corrosion [3-4].

In the present work, the impact of nitrates on the reduction and oxidation mechanisms of the silicon-rich stainless steel in concentrated and hot nitric acid has been investigated using electrochemical techniques (Linear sweep voltammetry, chronoamperometry, electrochemical impedance spectroscopy) coupled with surfaces analyses (SEM, XPS,…).

Linear polarization curves (Figure 1) show the influence of nitrates at boiling temperature. Despite a constant proton concentration, current and corrosion rate increase with the addition of nitrates to the medium. Nitrates are directly involved in reduction mechanisms of nitric acid, which can explain the increase in the cathodic current. It seems that nitrate ions could also play a role in the anodic dissolution of the considered alloy as the anodic current is significantly enhanced. Further experiments were performed by examining the variation of the oxide layer properties. XPS measurements show variations in the oxide layer formation depending on nitrates concentration.

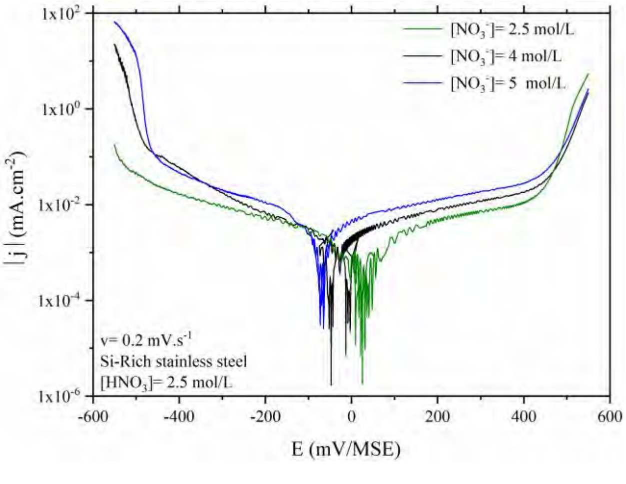

Figure 1: Linear polarization curves of the Si-rich stainless steel in nitric acid media $[H^+]_{fixed}$=2.5mol/L with different nitrate concentrations at boiling temperature. v= 0.2 mV.s^{-1}

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Understanding Electrochemical Oxidation of Methylguanines - Theory and Experiment

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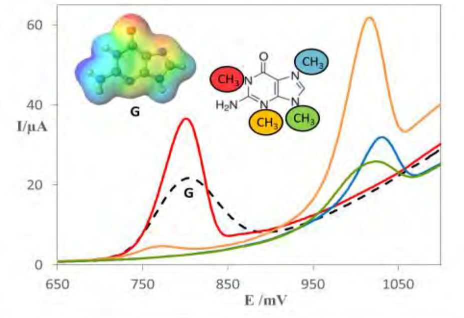
The oxidation of guanine (G) plays a major role in the redox processes of DNA due to the relative ease with which this nucleobase may be oxidized [1,2]. The general mechanism of G oxidation has been examined on different graphite electrodes depending on the environment, such as pH, ionic strength, and the type of a supporting electrolyte [3-5]. In our study, we show how the established mechanism is changing when G will be methylated. We investigated the oxidation processes of four N-methyl derivatives of G (1N, 3N, 7N, and 9N) on a polymer pencil graphite electrode (pPeGE) [6] to ascertain the relationship between the position of the methyl group and the corresponding oxidation behaviour. In the context of the oxidation peak potentials it was found that energetically easier oxidation can be expected in the case of methyl substitution at the pyrimidine ring rather than at the imidazole one. The position of the methyl affects the rapid protonation/deprotonation and tautomeric equilibria that are present in the oxidation processes. The assumption was proved by our theoretical study. The voltammetric data were completed with quantum chemical calculations: (i) the HOMO energies of all N-methylGs, (ii) the SOMO energies of the corresponding cations, and (iii) the theoretical oxidation potentials obtained from thermochemical cycles. Possible tautomeric structures of all the methyl derivatives were optimized using COSMO solvation models at B3LYP/6-31+G(d) level [7]. While 1-, 7- and 9-mG tautomers of lowest energy resemble G, guanosine and GMP derivatives in the sense that their species have hydrogen atoms located on N1 and N9 atoms [8], 3-mG prefers to have N7 atom protonated. This finding will be discussed in more detail with respect to specific electrochemical properties of 3-mG reported from experiments.



The voltammetric oxidation signals of N-methylguanines on a polymer pencil graphite electrode (pPeGE); the ESP map of G (the isosurface level = 0.03).

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Understanding the Reconstruction of Ni Nanoparticles on N-Doped Carbon Materials

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The development of efficient and selective electrochemical carbon dioxide reduction reaction (eCO_2RR) catalysts is an important but challenging task. Metal-nitrogen-carbon (MNC) materials, where the single metal atom is coordinated to pyridinic or pyrrolic nitrogen atoms, are promising candidates to achieve high activity and selectivity towards CO and can proceed to alcohols and hydrocarbons. Among them, the Ni derivative (NiN_xC) exhibits the highest efficiency for producing CO, at the different potentials and industrial current densities. [1,2]

The variation in the synthesis of defects can change the surrounding electronic structure and coordination environment of metals, where directing features are the size of vacancies and N unsaturated and saturated coordination sites. The metal can change its oxidation state depending on these variables. Therefore, the need for different potentials. Furthermore, it has been shown that Ni nanoparticles supported on carbon materials can reach the same selectivity as single-metal atom catalysts when the reaction is consistently performed under electrochemical condition.[3]

In the present work, with Density Functional Theory (DFT) we focus on the Ni nanoparticle reconstruction, taking CO_2 reduction as an example. We have evaluated the activity and selectivity of potential NiN_xC active sites together with the reconstruction and redispersion of supported nanoparticles under electrochemical conditions. We show that such reconstruction occurs due to the disintegration of $Ni(CO)_x$ complexes on low N saturated materials. The selectivity, on the other hand, is higher on N saturated materials.

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The Polymer Pencil Graphite Electrode – the Most Sensitive Tool for the Simultaneous Determination of Purine Metabolism Products

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Xanthine (XA), hypoxanthine (HXA) and uric acid (UA) are degradation products of purine metabolism. It is commonly known, that abnormalities of the metabolite concentrations in human serum and urine are sensitive indicators of many disorders, such as gout, xanthinuria, hyperuricemia, and perinatal asphyxia. The detection and quantification of XA, HXA and UA in body fluids is very important in the study of homeostasis of the xanthine oxidase (XOD) system and clinical diagnostics [1, 2]. Many techniques were developed for the simultaneous determination of the purine degradation products, e.g. enzymatic methods [2 ,3] high-performance liquid chromatography (HPLC) [2, 4, 5], capillary electrophoresis (CE) [2, 6], and also electrochemistry based methods [2, 7-14].

In the context of electrochemistry, it has been shown that the oxidation processes of purines can be observed and studied using different types of graphite electrodes, e. g. pyrolytic graphite, polymer pencil graphite electrode (pPeGE) or screen printed graphite electrode (SPGE), with good reproducibility. In addition, this electroanalysis is fast, cheap and applicable in medicine and food industry.

The aim of our research was the electrochemical determination of HXA, XA and UA at chosen graphite electrodes by using linear sweep voltammetry (LSV) and cyclic voltammetry (CV) in connection with the elimination voltammetry with linear scan (EVLS). The oxidation behaviour of the above-mentioned purine derivatives was investigated not only with respect to pH (pH 2-9; phosphate – acetate buffer) and (micromolar and submicromolar) concentration but also with respect to the type of the graphite electrode used (pPeGE – polymer pencil graphite electrode, BPPGE - basal plane pyrolytic graphite and EPPGE - edge plane pyrolytic graphite). As results from the voltammetric experiments, the oxidation behaviour of purine derivatives is strongly pH-dependent. However, the position of the oxidation signals of XA, HXA, and uric acid allows to distinguish these three important derivatives at all pH values. Based on the concentration dependences, it can be concluded that polymer pencil graphite electrode (pPeGE) is the most sensitive sensor for the determination of purine metabolites, as follows from the comparison of different types of graphite electrodes.

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Modeling and Simulation of All-Solid-State Batteries with Block Copolymers

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All-solid-state batteries (ASSB) are experiencing a growing scientific interest in recent years as potential next-generation high-voltage batteries with great intrinsic safety. Using polymer electrolytes in ASSBs can solve problems with current battery technologies, such as dendrite growth [1] and flammability [2]. Particularly with regard to mechanical properties and stability, polymers are promising compared to other solid electrolytes. A large number of different polymers are currently being discussed [3].

In this contribution, we investigate the processes in block copolymer electrolytes [2] by a multi-physics continuum transport model. The methodological framework for thermodynamically consistent modeling is given in previous work of Latz et al. [4].

The description of the polymer electrolyte material is based on the specific free energy, which includes contributions due to mechanics, configuration and polarization. For the configurational free energy, the Flory-Huggins solution model is applied to catch the entropic behaviour of a polymer solution. In contrast to transport theories of other electrolytes, we formulate our model with respect to the polymer velocity. This enables us to parameterize the model with data from simulations on the atomic scale, e.g. from molecular dynamics simulations [5].

We investigate the behavior of ASSBs with polymer electrolytes under different operating conditions and compare our simulations to experiments as well as simulations of other types of electrolytes. The most prominent differences are expected for the configurational and mechanical properties.

This is a first step towards the theory-based spatially and time-resolved description of processes in ASSBs with block copolymer electrolytes.

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Sensitive and Selective Detection of Pyocyanin with a Thermosensitive Hydrogel with Au/Ag Nanoalloy

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The rapid detection of bacterial strains represents a hot topic thoroughly discussed across the biomedical field. Together with the existence of nosocomial pathogen agents that impose extreme medical and financial challenges throughout diagnosis and treatment, the development of rapid and easy-to-use sensing devices has gained an increased amount of attention. Moreover, antibiotic resistance considered by World Health Organization one of the "biggest threats to global health, food security, and development today" enables this topic as high priority. *Pseudomonas aeruginosa*, one of the most ubiquitous bacterial strains, has various quorum sensing systems that are a direct cause of their virulence. One of them is represented by pyocyanin, a blue pigment with electroactive properties synthesized from early stages of bacterial colonization. Thus, the sensitive detection of this biomarker could enable a personalized and efficient therapy (1, 2).

A thermosensitive polymer, modified with Au/Ag nanoalloy was employed for the rapid and accurate detection of pyocyanin, a virulence biomarker of *Pseudomonas aeruginosa*. The sensor displayed a linear range from 0.12 to 25 μM, and a limit of detection of 0.04 μM (signal/noise=3) and was successfully tested in real samples spiked with the target analyte without any pretreatment other than a dilution step. The detection of pyocyanin with high recovery in whole blood in a time frame of 5-10 minutes from the moment of collection was performed with this electrochemical sensor.

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Electrochemical and in situ XAS/XRD Investigations of Nitride-Stabilized Non-Noble Metal Core - Pt Shell Nanocatalysts

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The inadequate activity and stability of Pt as a cathode catalyst under severe operation conditions are the critical problems facing the application of proton exchange membrane fuel cells (PEMFCs). Novel route to synthesize highly active and stable oxygen reduction catalysts involves deposition of Pt monolayer on an appropriate metal/alloy core. Platinum monolayer electrocatalysts offer ultimately low Pt content, complete utilization of Pt atoms and tunable activity induced by a suitable underlying structure [1]. Nitrogen atom in the core of the metal nitride (M = Fe, Co, Ni) nanoparticles covered by a thin Pt shell promotes the Pt ORR activity and provide a stabilizing effect under high oxidizing conditions suppressing the core dissolution during potential cycling [2]. Nitriding metal nanoparticles in ammonia enhances the corrosion resistance of the cores, and simultaneously encapsulating them by one to two Pt monolayer shells. $Pt_{ML}NiN$ core-shell nanoparticle was found to have properties that meet or exceed the DOE 2020 target.

The Synchrotron Catalysis Consortium (SCC) is partnered with the QAS and TES beamlines at the National Synchrotron Light Source II at Brookhaven National Laboratory to promote the utilization of synchrotron techniques for cutting-edge catalysis research under in-situ conditions. SCC provides dedicating facilities, in situ reactors gas, delivery and analysis systems and offers a variety of combined techniques including IR, Raman and electrochemical spectroscopies combined with X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) [3]. Electrochemical and *in situ* XAS and XRD experiments were conducted in the attempt to clarify processes of the formation of nitride cores and Pt shell during thermal annealing, the correlation to the activity to the core-shell structures and the effects of electronic states on the stability of the catalyst. Octahedral PtNiN was found to have excellent performance and improved stability over other Pt catalysts. As shown in the XANES spectra of Fig.1, electrochemical excursion into oxide region does not induce changes in NiN core as it is protected by the Pt shell. The catalyst is also stable to the accelerated electrochemical cycling test as shown by XRD spectra of Fig. 1.

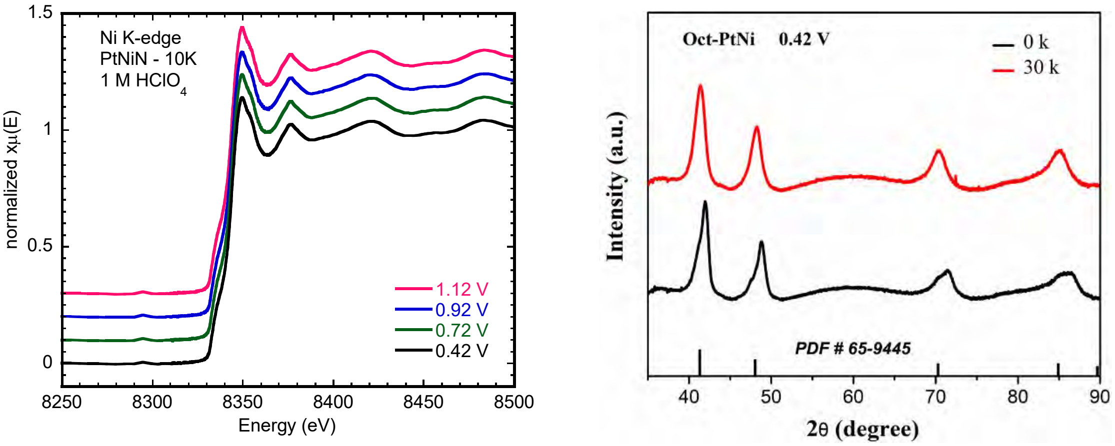

Fig.1 In situ spectra of PtNiN catalysts: XANES spectra after accelerated electrochemical cycling to 10,000 cycles and electrochemical excursion to oxide region (left), and XRD spectra of uncycled and cycled to 30,000 cycles catalysts at 0.42 V.

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Bridging the Gap Between Fundamental and Applied Fuel Cell Electrocatalysis Using a Gas Diffusion Electrode Half-Cell

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Although modern fuel cells are based on the utilization of solid membranes, fundamental catalyst research is mainly done in aqueous solutions via rotating disk electrode (RDE) or similar techniques. However, due to low solubility of reactant gases in those electrolytes mass-transfer limitation occurs at potentials relevant for the fuel cell operation. Hence, kinetic parameters are estimated in a narrow potential region of low currents and further extrapolations are required to achieve kinetic data in the relevant potential ranges. There are many open questions on the validity of such extrapolations. Therefore, in addition to RDE measurements, membrane electrode assemblies (MEA) tests are employed to evaluate catalysts in realistic fuel cell conditions. These experiments are complex (as they include a variety of different parameters), time-consuming and require large quantities of catalysts and expensive test equipment. To close the gap between fundamental and applied research intermediary testing methods need to be introduced, which combine the advantages of both approaches. Half-cell measurements using gas diffusion electrodes (GDE) have recently shown to be the most suitable method to enable high mass transport catalyst screening in relevant potential ranges and realistic electrode structures. [1, 2]

This work will concentrate on activity and stability evaluation for oxygen reduction reaction (ORR) catalysts. A proof-of concept on Pt/C GDEs reveals that, using this approach, current densities of up to 2 A/cm² can be achieved [3]. In contrary to other formerly used methods [2], it is possible to overcome mass transport limitations at relevant fuel cell operating potentials. The experimental shows good compliance with MEA experiments proving the method´s suitability for catalyst evaluation in realistic fuel cell potential ranges.

In a next step the method is transferred to alkaline media for the first time reported. [4] Thereby Fe-N-C cathodes with Aemion^{TM} ionomer are evaluated towards there ORR activity for anion exchange membrane fuel Cells (AEMFC). The impact of ionomer activation on the electrode's performance is revealed and the long-term stability of these non-noble catalyst layers in alkaline media successfully proven.

To gain deeper insights into stability of electrocatalysts in realistic electrode structures, the setup is coupled to an inductively coupled plasma mass spectrometer (ICP-MS). It will be shown that using solid electrolytes, the dissolution of Pt is minimized in comparison to aqueous electrolytes mostly used for stability experiments. This exhibits the necessity for intermediate techniques between MEA and RDE. Besides that, also the mobility of Pt-ions through Nafion is further investigated.

Thus, it can be concluded, that a new powerful experimental tool for decidedly catalyst layer evaluation for fuel cells or other electrochemical three-phase reactions (e.g. CO_2 reaction) is developed and successfully applied in fuel cell research. In the further development this approach will be transferred to enable high-throughput screening of catalysts. For this, a modification to a scanning flow cell (SFC) [5] setup is suggested. With this new device it is possible to rapidly screen the activity and stability of electrocatalyst layers depending on different material properties (e.g. catalyst loading gradients on one axis and structural property gradients such as pore size, ionomer content of membrane etc. on the other axis) using GDEs. Thus the most suitable electrodes under realistic fuel cell conditions can be worked out in a fraction of the time required for conventional methods.

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Towards stable catalyst layers for water electrolysis based on anion-exchange membranes

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Water electrolyzers based on anion-exchange membranes (AEMs) have gained attention in the last years due to promising cost reductions and greatly improved performances.[1] However, most anion-exchange ionomers still lack stability, as membranes and specifically when employed as a binder in the catalyst layers upon AEM water electrolyzer (AEMWE) operation.[2]

Here, we focus on the stability of catalyst layers for AEMWE and on measures to reduce the loss of catalyst due to poor adhesion and mechanical and hydrolytic stability issues of the ionomer binder. Fabricating catalyst-coated membranes (CCMs) using a spray coater allows the exact control of the layer-by-layer deposition rate of the catalyst layer on the membrane. By adjusting the deposition rate and hot plate temperature following experiences published recently by Klose et al. [3], as well as the ink composition, the stability of the catalyst layers was improved. As can be seen in (Figure 1 b), the catalyst layer integrity was mostly maintained after ion-exchange to the OH$^-$-form and exposure to water, while non-optimized spraying results in poor adhesion and areas without any catalyst (Figure 1 a). To quantify and compare the degradation of full MEAs under operating conditions short-term current holds and performance evaluations were performed in a water electrolyzer employing 0.1 M KOH at 60 °C (Figure 1 c). This work summarizes the recent achievement in the establishment of a stable AEMWE based on Aemion™ ionomer.

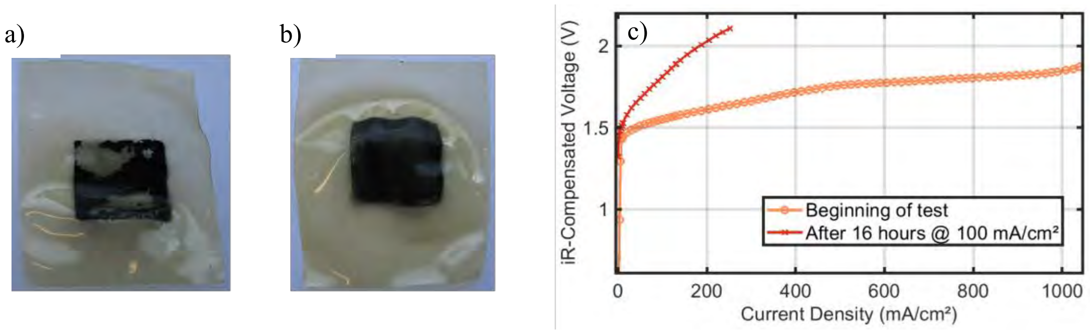

Figure 1: The IrOx catalyst layer sprayed on an Aemion™ membrane shows significant loss of catalyst upon ion-exchange to the OH$^-$-form and subsequent washing with deionized water (a), while optimized spray parameters result in a maintained cover with catalyst (b). This instability of the catalyst layer also contributes to the degradation observed when measuring CCMs in an AEM water electrolyzer overnight, as indicated by the changes in recorded polarization curves (c).

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Rheological changes of polypyrrole films from “salt in water” to “water in salt” solutions

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Pseudocapacitive materials, together with carbonaceous ones, hold the promise for high-performance electrochemical capacitors, since they display high energy density due to fast faradaic reactions on electrode surface (pseudocapacitive processes)[1]. Among them conductive polymers (CP) figure as interesting materials, since they present many advantages as low cost, high voltage window and redox activity, being the last one dependent on chemical modifications[1]. However, CP major disadvantage consists of polymeric chains structure breakdown along redox process, due to volumetric changes caused by ions and solvent exchange. Such fading compromise CP-based device cyclability[1]. Several attempts were made to circumvent it, such as 3D nanostructuring and CP-carbon composites[1]. Nevertheless, solvent effects seem to be scarcely explored. In this sense, the present work explores the volumetric changes of Polypyrrole/Dodecylbenzenesulfonate (Ppy/DBS), assisted with electrochemical crystal quartz microbalance with dissipation (EQCM-D), in traditional “salt-in-water electrolyte” and other one “water-in-salt electrolyte” (WiSE)[2], both based on LiTFSI salt. EQCM-D measurements shown that, in LiTFSI 1.0 mol L^{-1} solutions, Ppy behaves as a viscoelastic film during oxidation (high dissipation (ΔD) values) and contrary during reduction. Such viscoelastic change is attributed to water exchange during oxidation and the variation of film stiffness. On the other hand in WiSE, the same film behaves as a rigid one ($\Delta D \sim 0$), showing that, in WiSE, solvent exchange barely affects film stiffness and indicates lower volumetric changes. To explore that effects, the motion of freestanding PPy/DBS in both electrolytes were studied. Since it is well known that such movements mainly stems from water exchange[3]. Figure 1 shows the bending angles differences during oxidation and reduction for PPy at both electrolytes. It is noticeable that PPy bending in WiSE is negligible in comparistion with the one in LiTFSI 1.0 mol L^{-1}.

Figure 1: Freestanding Ppy films bending angle at LiTFSI 1.0 mol L^{-1} (left) and LiTFSI 7m (right)

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FAPESP grants: TTO (17/10046-9),VLM (13/22748-7) MML (19/02669-1)and 15/ 26308-7, CNPq and CAPES

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Tetracycline Detection Using a Gold Nanostructured Electrochemical Aptasensor

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Tetracycline (TC) is one of the most common used antibiotics for the treatment of infectious diseases in veterinary medicine and due to its high accumulation, important levels can be found in animal based products and environmental samples [1]. Therefore, there is an imperative need to develop highly sensitive and selective methods with easy operation and *on-site* applications for TC.

An electrochemical sensor for TC selective detection based on a gold nanopatterned platform and DNA-sensing strategy was developed.

Firstly, gold was electrodeposited on glassy carbon electrodes, after a previous polystyrene beads deposition, from a $HAuCl_4$ solution to obtain a 3D-nanostructured gold nanovoids (AuNVs) platform (**Fig.1**). The platform generation steps were optimized to obtain the best platform design which was characterized by electrochemical (CV, EIS) and microscopy analysis (SEM, AFM, EDX).

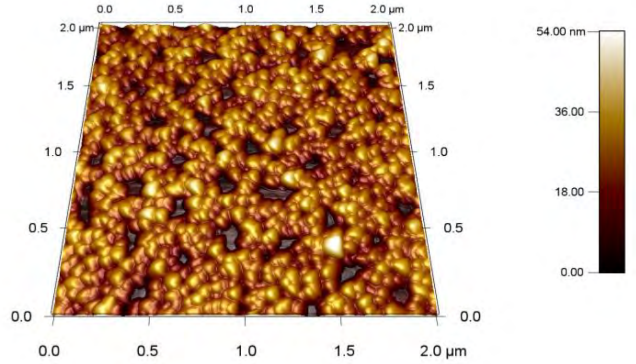

Fig. 1. AFM image of the Au-nanovoids platform resulted after the polystyrene dissolution.

A thiolated Ferrocene-labelled DNA sequence specific to TC was further covalently immobilised on the optimized AuNVs/GCE platform. Different strategies for Fc-DNA immobilization at AuNVs/GCE platform were investigated; multipulse amperometry (-0.5 V to +0.2 V profile pulses for 10ms, 32s total time) showed the highest peak intensities in terms of Ferrocene signal I(µA)/STDEV ratio. The next step was represented by the free active gold binding sites blocking using an unspecific short-thiol was electrochemically immobilized at the Fc-DNA/AuNVs/GCE platform, followed by the affinity reaction with TC. The optimized sensor was able to selectively detect TC in the nanomolar range with very low interference from similar antibiotics. A signal-off ferrocene-labelled DNA-sensor for tetracycline detection was developed based on a gold nanopatterned platform and possible applications on sewage, river and food samples will be presented.

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Application of the Co-Mo-Cu coatings as cathodes for hydrogen evolution reaction

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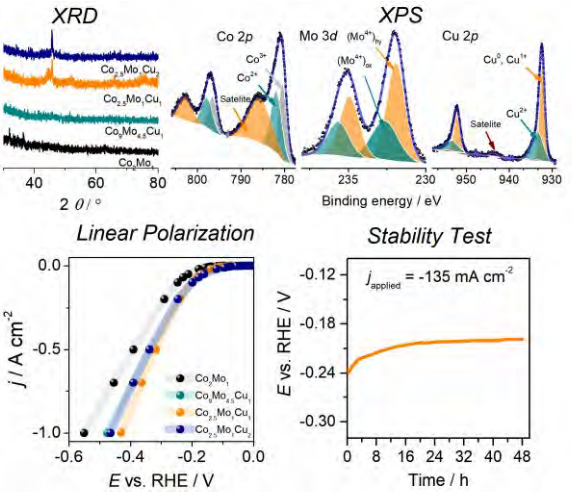

The most of energy expended in the world originates from fossil fuels. However, it is expected the future shortage of these fuels as a result of the depletion of oil sources. Besides that, the high consumption of petroleum derivatives discharges a huge amount of toxic and polluting substances for the environment. In this context, fuels with high energy densities and that do not harm the environment, for example, molecular hydrogen (H_2) are indicated as ideal substitutes for petroleum products.[1,2] This work reports the investigation of the electrodeposition of Co-Mo and Co-Mo-Cu coatings as a catalyst for the hydrogen evolution reaction (HER). Four deposition baths were proposed in the molar ratios of 2:1:0, 2:1:0.01, 1.5:1:0.05, and 1.5:1:0.2 of Co:Mo:Cu using sodium citrate as complexing agent and pH 8.7.[3] Co-Mo-Cu coatings were obtained in constant current of -30 mA cm^{-2} for 40 min on a glass embedded 1010 steel billet substrate with a 0.2 cm^2 exposed area. The electrocatalytic activities of the coatings were evaluated by stationary cathodic polarization curves (and Tafel curves), electrochemical impedance spectroscopy (EIS) and continuous electrolysis in 6.0 mol L^{-1} KOH aqueous solution. The amount of cobalt, molybdenum, and copper in the coatings varied from 67 to 43, 33 to 22 and 35 to 7 at. %, respectively. Co-Mo deposit exhibited a smooth morphology with spherical nodules and cracks across the surface. On the other hand, Co-Mo-Cu presented an irregular surface with well-defined grains, which are in rounded sha of different sizes. The XRD diffractograms with few peaks suggesting that all coatings present an amorphous or nanocrystalline structure, even though the peak near to 45° is correlated for fcc cobalt. The XPS analysis showed that Co, Mo and Cu are present on the surface of the coating. The deposit obtained in the molar ratio bath 2:1:0.05 of Co:Mo:Cu showed better activity for HER, with current of the order of -100 mA cm^{-2} obtained in only -200 mV overpotential. In addition, Co-Mo-Cu coatings exhibited excellent HER stability. At 48 h continuous electrolysis at -135 mA cm^{-2} the potential varied only 3.7% for more positive potentials. The slopes of Tafel near 40 mV dec^{-1} and the EIS experiments indicated a Volmer-Heyrovsky type mechanism with Heyrovsky being the rate-determining step.

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Conducting Polymer Nanocomposites: Electrochemical Characterization and Application for Arsenic Detection

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In the last couple of years, most of the work was devoted to synthesize new sensing nanocomposites to improve a sensor performance in terms of sensitivity, selectivity, and biocompatibility. Of those synthesized nanomaterials, conducting polymer composites have been widely used in the construction of sensor surfaces. Several conducting polymers *i.e.* polythiophene, polyaniline, polymethylene blue, polyanthranilic acid, polypyrrole, and poly(o-phenylenediamine) display advantages due to their charge transport properties and electrochemical redox efficiency, which are attributed to the delocalization of π-electrons over the polymeric backbone [1, 2].

For a greater enhancement of the electrochemical sensor performance, different electrode systems have been developed based on surface modification with nanomaterials. The synergy of multifunctional materials, recognition elements, and electrochemical methods is improving the selectivity, stability, and reproducibility, thus promoting the development of sensors for assays and bioassays.

Polyaniline (PANI) was used to obtain a nano/micropatterned surface at graphite screen printed electrodes (GSPEs) with applications in the biosensors field. The obtained polymeric film was electrochemically characterized by cyclic voltammetry and electrochemical impedance spectroscopy in different redox probes. Different architectures were obtained by depositing noble metal nanoparticles (AuNPs, PtNPs, Au-PtNPs) at the modified electrodes and the performance of the hybrid composites was assessed. An application of the newly developed polymer-based electrodes will be presented.

Arsenic (As) is one of the most abundant mineral and one to the most toxic compounds. The chronic exposure to arsenic can cause DNA mutation, which can lead to aberrant gene expression and carcinogenesis. Platforms based on Au-PtNPs/GSPE and Au-PtNPs/PANI/GSPE were tested for direct detection of As[III] by means of square wave anodic stripping voltammetry(SWASV). The first platform allowed the As(III) determination in the range of 0-200 nM As(III) while the second one in the range of 0.1-1.25 mM As(III). Interference studies were performed in the presence of Cu(II), Pb(II), Hg(II). Novel and easy to use nanohybrid platforms based on a mixed film of PANI and bimetallic composite Au-PtNPs for As(III) electrochemical fingerprinting was obtained [3].

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Operando X-Ray Analytics and Electrochemical Characterization Illuminate SOFC Perovskite Materials

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Solid oxide fuel cells (SOFC) represent a key technology for the transition to renewable sources of energy due to their high efficiency. The main advantages of SOFC compared to other fuel cells are the use of non-precious metal electrodes and fuel versatility. Nonetheless, the high operation temperatures lead to degradation processes and the need for expensive materials, thus much effort is focused on reducing operation temperatures [1]. Two main approaches involve the use of proton conductors as electrolytes and nanoparticle exsolution from mixed ionic and electronic (MIEC) electrodes [2,3]. SOFC work under high temperature, oxidizing/reducing atmospheres and under polarization potential. These conditions greatly affect properties such as the electronic and atomic structure of electrode surfaces and electrode/electrolyte interfaces. In this sense, the combination of complementary advanced characterization techniques for *operando* studies is essential to understand the complex processes occurring on the fuel cell components.

In this work, the two aforementioned approaches to lowering SOFC operation temperatures are addressed: The nanoparticle exsolution processes in $Sr(Ti,Fe)O_{3-\delta}$ (STF) and Ni-doped STF (STFN) MIEC electrode model cells are studied using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and electron-yield X-ray absorption spectroscopy (AP- XAS) in combination with electrochemical impedance spectroscopy (EIS) and electrode polarization. These techniques give information on the surface chemistry of the electrodes under reducing and oxidizing atmospheres at device operation temperatures, allowing to follow nanoparticle exsolution processes, its reversibility, and its effects on the electrode performance. The second approach, the use of proton-conducting electrolytes, is examined in a study of $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ (BCZY) proton conductors by a combination of in-situ X-ray diffraction combined with EIS, taking advantage of the H/D isotopic effect to determine the range where this electrolyte is a pure proton conductor and where it coexists with O-ion conduction. Furthermore, neutron-based techniques, such as neutron powder diffraction (NPD) and quasi-elastic neutron spectroscopy (QENS) were used to elucidate the crystalline structure and proton transport mechanism, respectively.

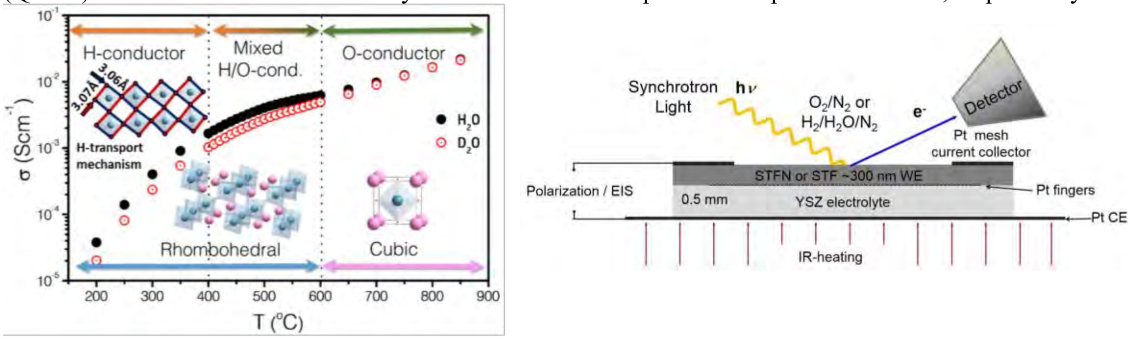

Figure 1. a) BCZY conductivity vs. temperature under H_2O- and D_2O-containing atmospheres and rhombohedral-to-cubic phase transition, and b) STF/STFN cell setup for *operando* characterization.

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Enhancement of Electrocatalytic Formic Acid Oxidation on Au(111) by the Pyridine Group

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The use of structurally well-defined Au(111) electrodes allows for a better understanding of the influence of adsorption processes on electrocatalytic reactions. The formic acid oxidation (FAOR) on Au(111) electrodes exhibits current density-potential curves indicating a self-inhibition due to the blocking of active sites by strongly adsorbed formate (Figure 1a, blue curve) [1]. Similarly, the specific adsorption of phosphates also lowers the activity [2]. For platinum electrodes, the presence of bismuth adatoms leads to a CH-down adsorption of formate facilitating the abstraction of the hydrogen atom, which is supposed to be the rate determining step of the reaction [3]. The systematic modification of the electrode surface by adsorption of suitable molecular species allows to influence the adsorption behavior of formate and to tailor the interfacial structure.

In this study, the effect of two prominent organic adsorbates, pyridine (Py) and 4-mercaptopyridine (4-PyS) on the FAOR on Au(111), is discussed. Both molecules form ordered adlayer structures in the potential range where the electrocatalytic reaction occurs [4,5]. The irreversibly adsorbed 4-PyS (S-bonded) exposes its pyridinic nitrogen to the solution, which leads to an enhanced activity towards FOAR. The hysteresis observed for the positive and negative potential sweep is due to a change in configuration of the adlayer (Figure 1a, red curve). The significance of the pyridinic nitrogen for the reaction mechanism is stressed by the comparison with the strongly blocking and inactive thiophenol (black curve). While pyridine is reversibly adsorbed with the nitrogen bonded to the Au(111) surface, it causes a surprisingly strong enhancement in FAOR activity (Figure 1b, compare red and blue curve) [5,6].

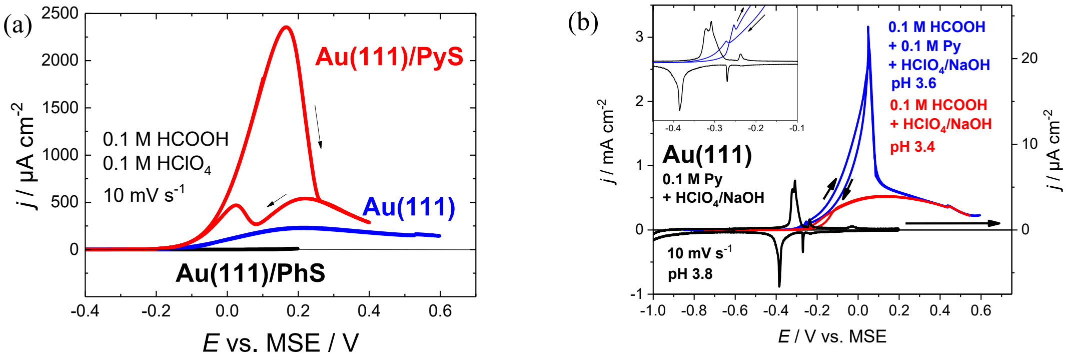

Figure 1: (a) Comparison of current density-potential profiles for SAM-modified Au(111) surfaces in 0.1 M $HClO_4$ + 0.1 M HCOOH. While 4-mercaptopyridine (PyS) enhances FAOR, thiophenol (PhS) inhibits the reaction.

(b) Current density-potential curves for formic acid oxidation on Au(111) in 0.1 M HCOOH + 0.125 M NaOH + 0.075 M $HClO_4$ (pH 3.4, red curve) and for Au(111) in 0.1 M pyridine + 0.1 M HCOOH + 0.05 M $HClO_4$ + 0.1 M NaOH (pH 3.6, blue curve) at a scan rate of 10 mV s^{-1}. The black curve displays the behavior of Au(111) in 0.1 M pyridine + 0.3 M $HClO_4$ + 0.2 M NaOH.

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Model-based and Experimental Analysis of Inhomogeneous Gas Diffusion Electrodes by EIS

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Gas diffusion electrodes (GDE) are utilized in many technical applications in order to avoid an early limitation by mass transport. An example is given by oxygen depolarized cathodes (ODC), which are used in advanced chlor-alkali electrolysis and enable high current densities despite the poor solubility of the reactant oxygen in the liquid electrolyte. As shown lately, the composition and structure of ODCs is of high importance for achieving small potential losses and high limiting current densities [1]. Furthermore, it has been shown that the electrode structure as well as the position of the three-phase boundary within the ODC are highly inhomogeneous [2].

In this work, the influence of the ODC structure on the performance is investigated. Electrochemical Impedance Spectroscopy (EIS) spectra and polarizations curves were recorded for ODC with various binder and silver catalyst compositions. A dynamic one-dimensional three-phase ODC model [3] has been extended to simulate the influence of an inhomogeneous electrode structure. The model considers inter alia Tafel-equation for kinetics, Nernst-equation for open circuit potential, Stefan-flow in the gaseous phase, Maxwell-Stefan-diffusion in the liquid phases as well as the oxygen dissolution by Henry's law and the water evaporation by Raoult's law.

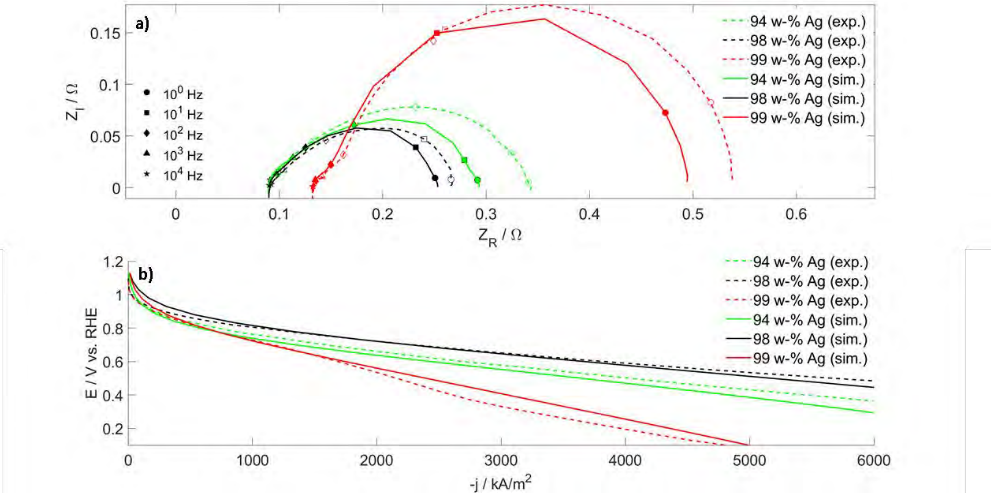

Fig. 1: a) Simulated (-) and measured (--) a) EIS at 2 kA m^{-2} and b) polarization curves of ODC with different catalyst contents.

The polarization curves show high limiting currents densities, whereas the EIS indicates relatively high charge transfer resistances. These contrasting observations are explainable by the inhomogeneous electrode structure: Some pores are highly active, which leads to high current densities. Other pores show a poor activity, which increases the impedance and enlarges the measured charge transfer resistance. This behaviour is illustrated by the distortion of the semi-circles in the Nyquist-plot and can be reproduced well by the extended model (cf. fig, 1 a)). Since all processes are stimulated at high frequencies above 1 Hz, which is the frequency range of double layer charge, no influence of mass transport has been detected. A comparison of ODC of different composition leads to the conclusion that the main indicator for a high electrode performance is the size of the three-phase boundary. Due to these new insights, on the one hand the distortion of the semi-circles in the Nyquist-plot is understood; on the other hand based on the identification of inactive pores, a fundamental for further improvement of the ODC is laid.

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MicroRNA Detection on Microsensor Arrays by SPR Imaging Measurements with Enzymatic Signal Enhancement

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Oligonucleotide detection-based tests, including safety screening for environmental chemical toxicity and healthcare management, are increasingly being adopted in the fields of environmental and biological evaluation. Micro RNAs (miRNAs), short non-coding RNAs with a length of 20–25 bases, have recently been attracted as biomarkers for potential applications to evaluation of stresses caused by environmental chemicals and diagnosis of lifestyle-related diseases or cancers. Rapid and simple detection methods are needed to permit the application of these miRNA detection tests in these fields as fast screening tools.

In this study, we investigated sequence-specific and simultaneous miRNA detections by surface plasmon resonance (SPR) imaging measurements on SPR chips possessing an Au spot array modified with probe DNAs based on a miRNA-detection-selective SPR signal amplification method. SPR chips were fabricated by deposition of Au/Cr thin films to a mechanically polished glass covered with a stencil template of the SPR chip pattern (16 spots with diameters of 0.8 mm). The Au spot surfaces were modified with DNA-NH_2_miR17 and DNA-NH_2_miR21 as probe DNAs (targeting miRNA biomarkers of hsa-miR-17 and hsa-miR-21 for lung cancer, respectively), mPEG-NH_2 (a negative control), and A_{30}-NH_2 (a positive control).

When the fabricated SPR chips were soaked in 5 μM hsa-miR-21, only DNA_miR21 (a complementary probe)-modified spots showed a sequence-specific SPR signal. Extension reaction of polyadenine (poly(A)) tails by poly(A) polymerase selectively enhanced this signal. The difference of the SPR signals between complementary and non-complementary probes amplified about five times before and after the poly(A) extension. For more sequence-specific SPR signal enhancement, we used a ternary complex of T_{30}-biotin/horseradish peroxidase (HRP)-biotin/streptavidin. Binding of the complex to the poly(A) tails showed larger responses for spots of the complementary probe than those for the positive control. In contrast, responses for the non-complementary probe and negative control were revealed to be quite small.

Then, oxidation reaction of tetramethylbenzidine (TMB) via HRP was utilized to enlarge the observed SPR signal. The SPR signal for the complementary probe remarkably increased, while those for the non-complementary probe and negative control slightly increased. These results show TMB was oxidized on HRP of the ternary complex to be changed to blue precipitation of Ox-TMB. The difference of SPR signals between the complementary and non-complementary probes showed another 4.5 times-amplification. We concluded that this process sequence-specifically and dramatically amplified the SPR signals. Moreover, further experiments of dependence of SPR signal on concentrations of miRNA solutions revealed the detection limit of this method is the attomole (10^{-18} mole) level. This is a simple, cost-effective, and feasible signal amplification method based on the organic compound TMB instead of metal nanoparticles.

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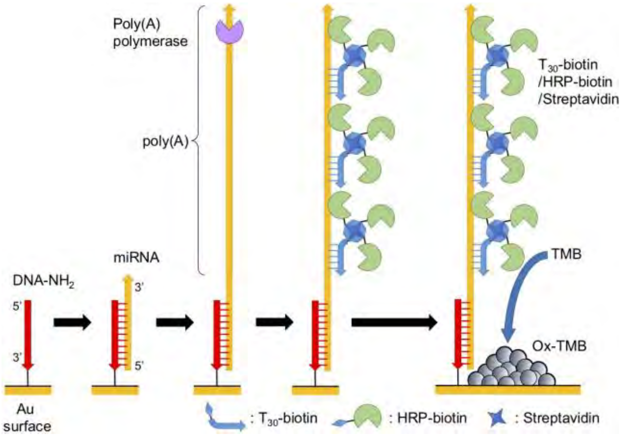

Fig. 1. SPR signal amplification process based on enzymatic reaction.

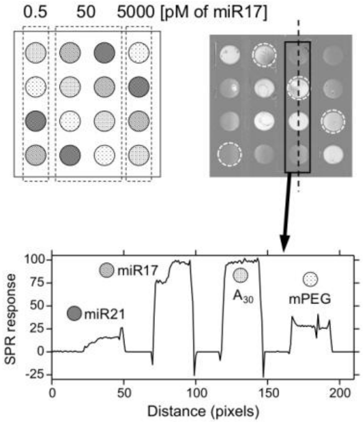

Fig. 2. Layout of spot modification on a SPR chip. SPR image and response to a miRNA

Detecting oxygen in catalyst layers by scanning electrochemical microscopy (SECM)

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Scanning electrochemical microscopy (SECM) is a powerful scanning probe technique for tracking the local electrochemical activity of an electrolyte-immersed substrate, by employing an ultra-micro-electrode. As the Thin Layer Electrochemistry regulations apply for the SECM setup, high spatial and time-related resolution is obtained, providing the SECM with the ability of being employed in various applications in the fields from biology to energy materials.

In this research SECM feedback mode is used to detect the presence of excess of oxygen in the catalyst inks drop-casted on an electrode. Catalyst inks containing either carbon supported Pt nanoparticles or carbon black were drop-casted on a glassy carbon electrode, with Nafion ionomer as binder.

SECM approach curves obtained by ORR-potential biased Pt tip (a = 12.5 μm, RG = 8) displayed positive feedback type behavior when approaching electrodes covered with catalyst layers, both in H_2SO_4 and KOH solutions (Figure 1). Approach curves on clean glassy carbon electrode showed negative feedback. As it is unlikely that true positive feedback would be observed on a catalyst layer, these measurements indicate that the increase in the tip current when approaching the catalyst layer results from excess oxygen present in the catalyst layer due to hydrophobicity or the porous surface structure of the layer. A similar observation has been reported when approaching a porous poly(vinylidene fluoride) membrane[1,] or CNT-based catalyst. As the tip depletes oxygen from the solution, oxygen from the porous film partitions into the solution, resulting in similar behavior to that observed when approaching a water–air interface. Simulations were performed to reproduce this effect.

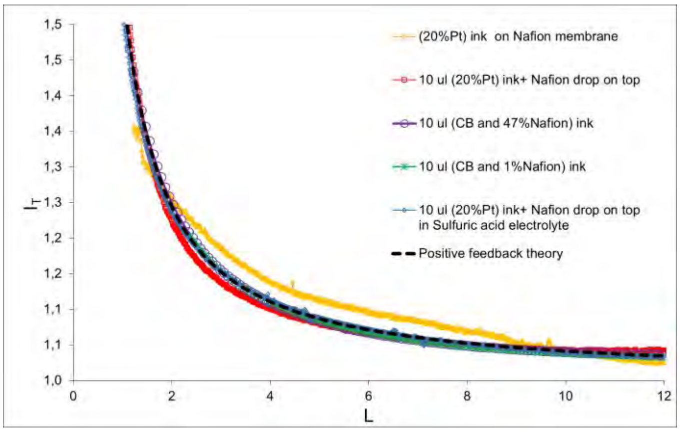

Figure 1. Theoretical Positive feedback curve and approach curves of different catalyst layers, in KOH and H_2SO_4 electrolytes.

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Performance Improvement of PEM Water Electrolyzer Anodes via a Bi-Functional Binder Polymer Blends for Ionic and Electrical Conduction

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Reducing the anode catalyst loading of proton exchange membrane water electrolyzers (PEMWE) is one of the major challenges for their mass commercialization[1,2]. In recent studies, the role of in-plane conductivity in low-loaded catalyst layers (CLs) has been studied intensively, suggesting that electrically isolated portions in the CL [2] and ionomer swelling during operation [3], result in higher resistances and hence lower catalyst utilization. We present a novel approach to reduce the CL in-plane resistivity by blending the proton conductive ionomer (Nafion) in the CL with an electrically conductive polymer (PEDOT:PSS). With this blend of ionomer and electrically conductive polymer we are able to increase the in-plane conductivity and reduce the contact resistances of a CL with an Ir-loading of 0.22 mg cm^{-2}. This results in a significant performance increase of a 120 mV lower overpotential at 3 A cm^{-2} compared to a conventional CL with ionomer only as binder and identical Ir-loading.

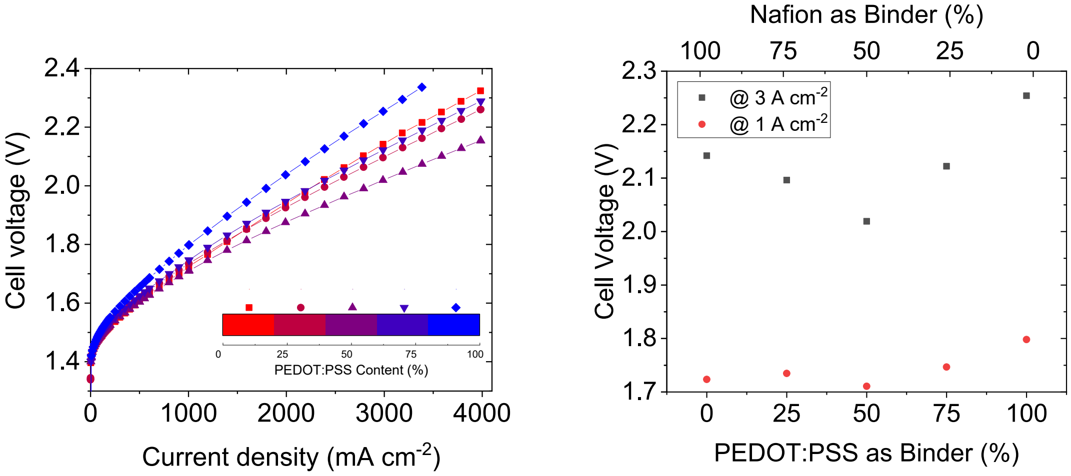

Figure 1 Blending of Nafion and PEDOT:PSS as a bi-functional binder in the CL resulted in lower overpotentials (left). The highest improvement was observed with a 50 % Nafion 50 % PEDOT:PSS blend (right). Operating conditions were: 80 °C, cathode and anode flowrate 40 ml min^{-1}, at ambient pressure, N115 membrane, anode loading of 0.22 mg cm^{-2} Ir and a cathode loading of 0.5 mg cm^{-2} Pt

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Improving the morphology and performance of all-hydrocarbon PEM fuel cell MEAs based on Pemion^{TM} ionomer

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Perfluorinated sulfonic acid-based ionomers (PFSAs) are the state-of-the-art proton conducting material in polymer electrolyte fuel cells nowadays. PFSAs, however, feature several drawbacks including the high cost, restricted operating temperature range, insufficient chemical stability and environmental hazard due to the use of fluorine-based chemistry[1]. Under these circumstances, several non-fluorinated hydrocarbon-based ionomers were introduced in recent years to replace PFSAs. A very promising candidate is a sulfonated phenylated polyphenylenes-based (sPPP) ionomer introduced by Skalski et al.[2]. The authors reported competitive MEA performance in comparison to a Nafion^{TM} membrane. In this work, we present different approaches to improve and engineer the electrode structure employing a sPPP-based ionomer (Pemion^{TM}) resulting in strongly improved performance of the all-hydrocarbon fuel cell[2]. This includes an adjustment of ionomer contents in the catalyst layers, as well as improved processing conditions of the CCM fabrication. This work reports electrochemical performance from all-hydrocarbon MEAs at different operating conditions, as well as ex-situ characterization via electron microscopy and dynamic light scattering.

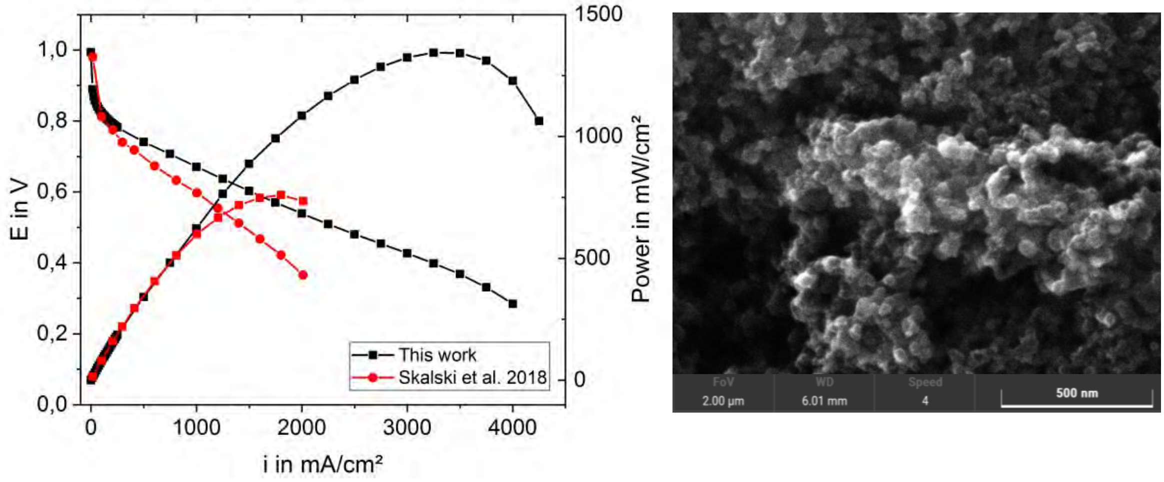

Figure 1 Elevated performance of PEMFCs (Pt-loading anode/cathode = 0.1/0.4 mg/cm²) with Pemion^{TM} (15 µm membrane thickness) in H_2/O_2 with a fixed flow of 0.25/1 l/min, 80°C, 95% r.H. and 1 atm (left) in comparison to literature (37 µm membrane thickness) and SEM micrograph of a CL with Pemion ionomer (right).

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Application of electrochemical approach and motility analysis in algal cells characterization

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This study aimed to examine the influence of the morphological characteristics of green algal cells on the adhesion process and their mobility. The used model organisms were *Tetraselmis suecica* and (Chlorophyceae), motile microalgae of micrometer size, with different morphological characteristics of the cell envelope. The *D. tertiolecta* cell consists cell membrane [1,2] enveloped by a glycoprotein cover (glycocalyx), while *T. suecica* cell consists of a cell membrane with complex theca made of scales, encrusted with calcium carbonate. *D. tertiolecta* cells have two flagella of equal length emerging from one basal body, whereas *T. suecica* cells have four flagella that pair out of two basal bodies.

Using the electrochemical method of polarography and chronoamperometry on a dropping mercury electrode, *D. tertiolecta* cells were characterized based on characteristic adhesion signals occurring over a wide potential range. *T. suecica* cells do not adhere to the charged electrode, which is a consequence of the compact cell envelope.

Using computer-assisted video microscopy and an Open Source Image Processing Software Icy (http://icy.bioimageanalysis.org/) cell swimming speed, the displacement length, and shape of their trajectories were quantified on 500 individual cells. Results showed that the speed of *T. suecica* cells is up to 4 times higher than that of *D. tertiolecta*, which is a consequence of a complex flagellar system.

Based on algal cell adhesion and motility characterization, the obtained results could contribute to a better understanding of the spatial distribution of green algal cells in the aquatic environment under stress.

Acknowledgment

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Synthesis of Nanoporous Anodic Alumina Architectures Involving Deep Eutectic Solvents for Supercapacitor Applications

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Self-standing nanowires arrays have shown great potential in a variety of important applications, including supercapacitors because of the high volume to weight ratio. They act as a current collector and as a substrate on which the active materials can be grown. Usually, controllable arrays of nanowires are obtained involving template assisted electrochemical deposition where nanoporous ordered aluminum anodic oxide (AAO) architectures represent the host matrix. Conventionally AAO patterns are produced through aluminum anodization in oxalic acid based electrolytes at low operating temperatures and relatively low anodic film growth rates. Low temperatures are preferred because the heat generated during anodization at high temperatures causes inhomogeneous growth of the porous AAO. In order to optimize the anodization process to form ordered AAOs, a quite novel approach involves the use of ionic liquids (ILs) as potential environmentally benign solvents and widespread application in materials chemistry and electrochemistry in a green synthetic strategy [1].

In this study, we aimed to bring insight to the synthesis of AAO architectures involving novel formulations of deep eutectic solvents based on eutectic mixtures of cholinium compounds, respectively of choline dihydrogencitrate/oxalic acid/ethylene glycol systems and comparing them with the anodic oxides formed in traditional aqueous electrolytes. The structural-morphological characteristics of the obtained AAO films formed under various operating parameters (i.e. anodization voltage, electrolyte temperature, anodization duration) were studied. The formed AAO architectures involving ILs were then used as patterns to electrodeposit Ni nanowires (Ni NWs) from aqueous solution at constant potential conditions. Afterwards, the surface of the Ni NWs was converted directly into $Ni(OH)_2$ involving the hydrothermal method [2]. The structure, composition and morphology of the obtained AAO, Ni NWs and $Ni(OH)_2$ were investigated by XRD, Raman and SEM techniques. The electrochemical performance of $Ni(OH)_2$ was studied by cyclic voltammetry and electrochemical impedance spectroscopy.
The influence of the AAO structural characteristics on the final self-standing Ni NWs and their electrochemical characteristics is also discussed.

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Cathodic Corrosion of Polycrystalline Au Electrodes: Applications in Electrocatalysis and Surface Spectroscopy

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Faceting and nanostructuring of polycrystalline Au electrodes by cathodic corrosion in concentrated aqueous alkali metal hydroxide electrolytes have been studied systematically. Scanning electron micrographs show the formation of octahedral Au nanocrystals and triangular pits by using NaOH and KOH solutions, respectively. These Au surfaces with preferential (111)-texture and a unique nanostructure are of special interest for new developments and applications in electrocatalysis and surface-enhanced Raman spectroscopy (SERS) [1,2].

Cathodic corrosion of Au leads to a single-crystal-like electrochemical behavior with characteristic features of Au(111) electrodes [3,4]. The electrocatalytic behavior of this new type of nanostructures will be presented for the hydrogen evolution reaction (HER) and for the formic acid oxidation reaction (FAOR).

The Raman activity of adsorbed pyridine on the nanostructured Au electrodes was studied with SERS. While untreated polycrystalline Au is not SERS-active, the use of cathodic corrosion opens up a way for *in-situ* applications of SERS in electrochemistry.

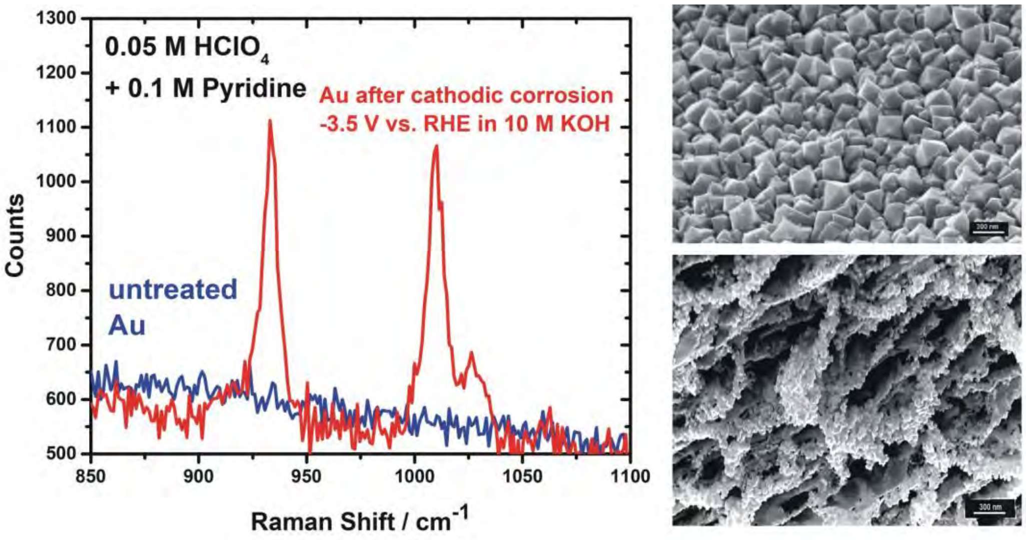

Figure 1: (left) Raman spectra of Au in 0.1 M pyridine + 0.05 M $HClO_4$ before and after cathodic corrosion in 10 M KOH with application of 3.5 V for 60 seconds. (right) Selected SEM micrographs of gold surfaces after cathodic corrosion.

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Electrochemical synthesis of graphene paper for supercapacitor application

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Graphene is a two dimensional material characterised by a honeycomb structure and sp2 hybridization that provides outstanding properties of this material. It can be prepared as a powder or as a porous monolithic structure (hydrogel or graphene paper). Graphene paper is characterized by high surface area, low weight, high electrical conductivity and furthermore it is a flexible and free-standing material, which makes it a perfect candidate for energy storage applications.

The objective of this research was electrochemical synthesis of graphene paper (ErGO) and its application in the flexible supercapacitor as freestanding active material. In order to obtain ErGO, graphene oxide (GO) paper was prepared by vacuum filtration or drop-casting while electrochemical reduction of GO paper was carried out by chromoamperometry method. During the reduction process GO paper was connected as working electrode by pressing a titanium road onto the paper. By using a number of techniques, including Fouirer-transformed infrared spectroscopy (FTIR), Raman spectroscopy, X-ray diffraction analysis (XRD) and conductivity measurement, it was shown that the reduction process was carried out successfully. The obtained ErGO papers were used for assembling supercapacitors with nickel current collector or supercapacitor with freestanding flexibile ErGO paper. The prepared supercapacitors were tested by cycling voltammetry and electrochemical impedance spectroscopy methods. The obtained results indicated good reversibility with specific capacitance of 44 F g^{-1}

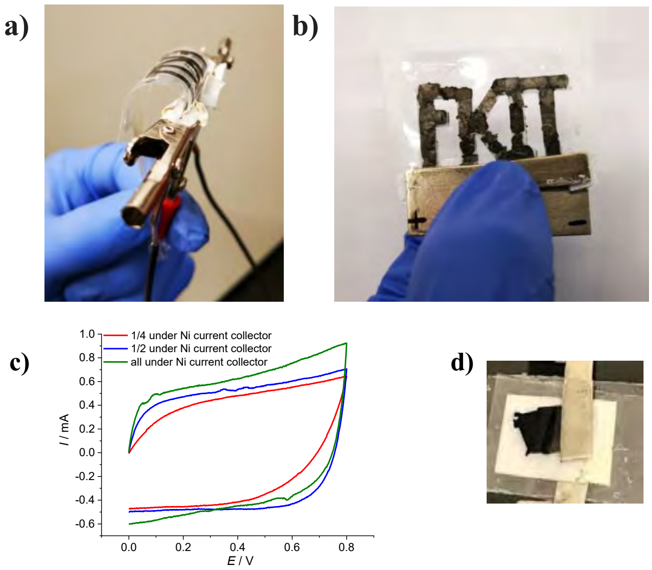

Fig. 1. Different forms of supercapacitors (a, b, d) and cyclic voltammetry response of freestanding ErGO paper or ErGO paper covered by Ni current collector (c).

Photoelectrochemical Degradation of Pharmaceutical Compounds at TiO_2/SnS_2 Electrode

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Pharmaceuticals are known to have a significant impact on aquatic environment causing ecological risk and human health damage. Accordingly, it is important to develop an innovative and practical water treatment technique, which will be able to remove them. Photoelectrochemical oxidation is one of the promising techniques due to its simplicity and combination of photocatalytic and electrochemical process. Additionally, recombination of photogenerated electron/hole pairs that occurs decreases by applying external potential, leading to enhancement in pharmaceutical degradation efficiency. One of the most important photocatalytic candidates is TiO_2. Since it is limited to UV-irradiation, significant efforts have been done to extend its absorption into the visible light region through TiO_2 doping or TiO_2 composite formation. Therefore, the aim of this work was to investigate photoelectrochemical activities of TiO_2/SnS_2 nano-composite. The examination was performed using photoelectrochemical techniques in 0.1 mol dm^{-3} NaCl solution, for degradation of pharmaceuticals such as diclophenac, salicylic acid and memantine hydrochloride. For this purpose, TiO_2/SnS_2 nano-composite was immobilised on FTO electrodes.

Good sensitivity of photocatalyst was shown by monitoring OCP in chopped light irradiation and by comparing EIS response in dark to the one under light irradiation. Electrochemical and photoelectrochemical degradation of pharmaceutical was monitored by linear polarisation. The experiments showed that it is possible to degrade pharmaceutical using electrochemical process and to improve degradation using solar irradiation for TiO_2/SnS_2 nano-composite electrode (Fig. 1). The obtained response is dependent on the on the type of pharmaceutical and its affinity towards the adsorption at TiO2-SnS2 surface [1].

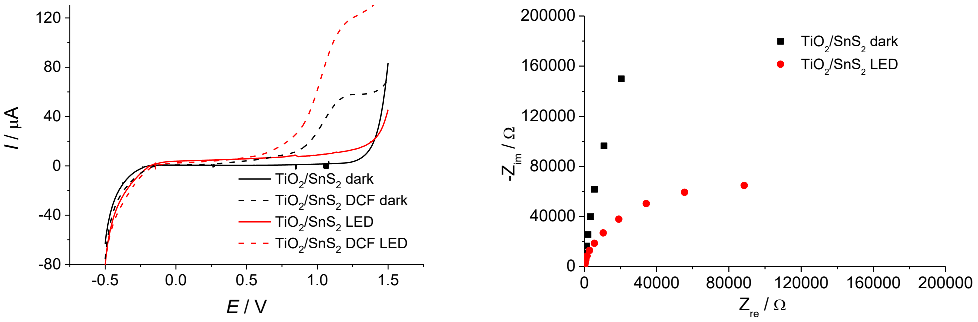

Fig 1. a) Linear sweep voltametry photocurrent response of TiO_2/SnS_2 in the presence and absence of diclofenac (DCF) and b) the Nyquist plot of TiO_2/SnS_2 composite in dark and under LED irradiation.

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Operando Investigation of Different Polysulfide Retention Approaches in Magnesium-Sulfur Batteries

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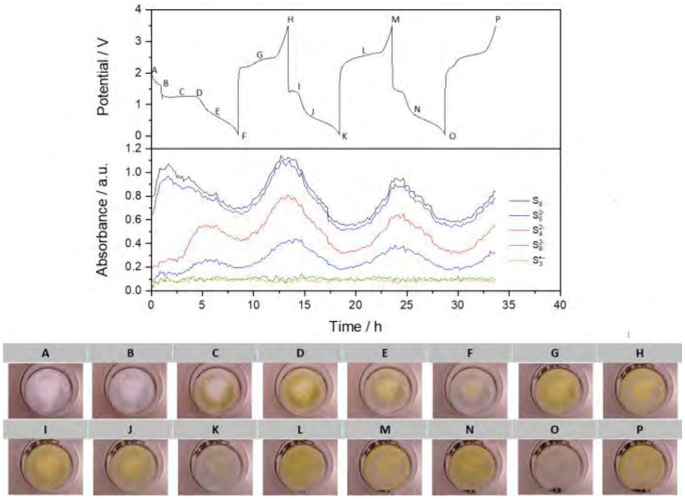
Since the first reported magnesium-sulfur (Mg-S) cell by Kim et al. in 2011 [1] interest in this post-lithium battery system has steadily increased due to its promising properties in regards of volumetric energy density, safety and costs. In recent years many research groups have attempted to unveil the underlying electrochemical mechanisms by sophisticated structure analysis of the solid product (MgS) [2] as well as spectroscopic investigations of the soluble intermediates (magnesium polysulfides, MgS_x) [3]. Analogous to lithium-sulfur (Li-S) batteries, the solubility of the latter causes the loss of active material and charge compensation through the polysulfide shuttle. Furthermore, the sulfur species contribute to the formation of an anodic SEI, which – in the case of magnesium metal – exhibits a rather passivating nature. This is supposed to be one of the origins for the fast capacity decay and the short cycle life of magnesium-sulfur battery cells.

Benefitting from previous Li-S research to retain sulfur species within the cathode and prevent the polysulfide shuttle, several retention approaches can be considered for the Mg-S system. Among the different strategies, the most promising ones are the sulfur incorporation in micropores, separator coatings with ionomers or carbons, covalently bound sulfur or the use of polar cathode additives as adsorption sites. In this study, the capability of selected attempts on magnesium polysulfide retention was investigated via *operando* UV/Vis spectroscopy and *operando* microscopy in optical cells. Besides the analysis of the separator coloration during galvanostatic cycling, the self-discharge during OCV was surveyed. In addition, significant influence of the electrolyte solvent and the polysulfide diffusion length on the reoxidation of the sulfur species was observed.



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Cysteine Self-Assembly on Au(100) Studied by *In Situ* STM, Voltammetry and DFT

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Functionalization of metal surfaces with organic molecules play key roles in biosensor fabrication, hybrid nanomaterials design, and controlled growth of nanostructures. Detailed understanding of the chemistry and dynamics involved can therefore lead to increased surface performance and control. Gold surfaces are widely used in catalysis and in molecular and biomolecular electrochemistry, where catalyst functionalization frequently relies on gold-sulfur chemistry.

We have explored monolayer formation and structure of cysteine (Cys), a natural amino acid that holds $-NH_3^+$, $-COO^-$ and –SH functionalities, on Au(100), which is much less studied than the other low-index Au-surfaces.[1] We have mapped the dynamics of Cys self-assembled monolayer (SAM) formation by a combination of open circuit potential evolution and kinetic Monte Carlo simulations. The structure of the SAMs is imaged using *in situ* scanning tunneling microscopy (STM) with single-molecule resolution supported by DFT calculations and STM contrast simulations (Figure 1). Unusual one-dimensional features were disclosed by the *in situ* STM images, unique to Au(100) and closely correlating with unique reductive desorption behavior (Figure 1b). Based on detailed analysis of *in situ* STM images and DFT calculation of Cys monomer and dimer adsorbates, we propose that the bright two-dimensional STM structures and high-energy reductive desorption peak represent Cys dimers. The dimers associate via two-prong electrostatic interaction between ammonium and carboxylate functional groups and bind vertically to Au(100) via a single Au–S bond leaving the other –SH group pointing away from the surface.

This level of molecular understanding of the chemistry involved in Cys SAM formation and structure is achieved by the combination of electrochemistry, microscopy and theoretical efforts, and can help to guide future electrochemical device design and gold nanomaterial functionalization protocols.

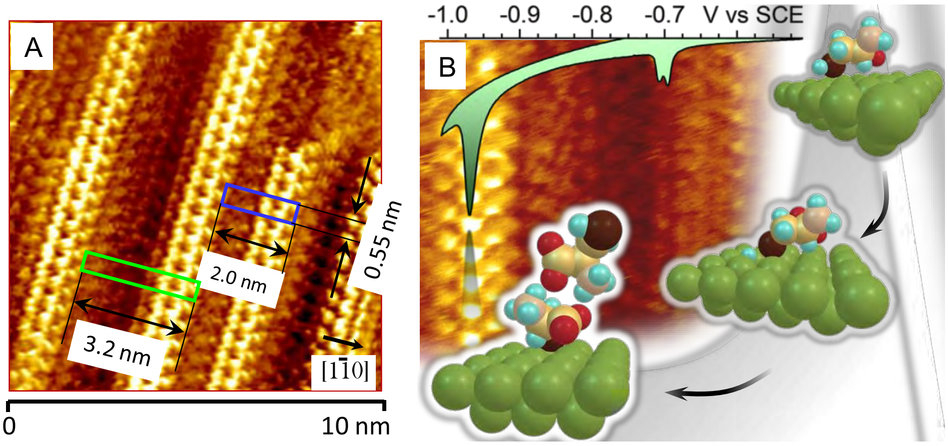

Figure 1. (A) *In situ* STM micrograph of L-Cys SAM on Au(100). Two distinct unit cells are observed highlighted with the green and blue squares. (B) CV of reductive desorption along with DFT simulations of L-Cys dimer formation.

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Bovine Serum Albumin Based Biosensor for Folic Acid Detection through Biomolecular Interaction Monitoring

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Folic acid (FA) is a bioactive food component whose deficiency can lead to a variety of health problems, while a high intake can reduce the cytotoxicity of natural killer cells. One of the most commonly used proteins in small molecules transport is bovine serum albumin (BSA). BSA interacts with these ligands at one or more of its sites, located in hydrophobic cavities. Herewith, the development of a BSA based biosensor for small molecule detection can be of great importance.

The binding mechanism of FA to free BSA was studied using fluorescence, while cyclic voltammetry and electrochemical impedance spectroscopy offer an insight on both the overall characteristics on the phenomena at the gold electrode surface (BSA binding to the electrode surface) and the detection of FA [1].

The fluorescence quenching mechanism of BSA by FA shows that there occurs a FA-BSA complex formation where one molecule of FA binds per one molecule of BSA, and the binding process is characterized by a moderate interaction with a binding constant of $K_b = 8.72 \times 10^4\ \mathrm{M}^{-1}$ at 25 °C. Knowing this, a BSA biosensor was used for electrochemical FA detection. Confinement of BSA to gold surfaces occurred through drop casting, inducing conformational changes, which influenced the orientation of BSA molecules binding sites towards free FA. Thus, the apparent binding constant calculated using electrochemical methods was 5 times higher, proving a stronger binding. Preliminary results show a sensitivity of 67 nA cm^{-2} $\mu\mathrm{M}^{-1}$, with a linear range up to 20 µM FA. These results enable further studies towards BSA-biosensor development for the detection of small molecules such as FA.

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The Impact of Bronze Composition on Properties of Self-Assembled Monolayers of Phosphonic Acids

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Self-assembled monolayers (SAMs) of long-chain organic acids are formed by adsorption of acid on the surface of oxide-covered metal, resulting in acid-base reaction between metal oxide and acid. This reaction is followed by the self-organization of alkyl chains which creates a very thin and compact film. Due to their unique properties, they are used in many fields, from nano fabrications, sensorics, electrocatalysis to microelectronics. In addition to the listed fields, they have also proven to be good corrosion inhibitors on various metal substrates. Given that corrosion is a significant problem globally, SAMs are emerging as a potential solution to this global problem.

There are many parameters in the preparation of SAMs that can influence the quality of the formed film, but in this work we will deal with the influence of the composition of the bronze substrate on their formation. More specifically, we will form films on pure copper and several bronzes of varying composition so that we can see how and to what extent individual alloying element affect the quality and arrangement of the SAMs. This information is important given that better arranged films provide stronger and longer lasting protection.

In order to obtain a compact well-ordered film which will provide long term protection, SAMs preparation procedures consist of bronze pretreatment and phosphonic acid adsorption by dip-coating followed with drying period. Protective properties of phosphonic acid SAMs are examined by linear polarization measurements and electrochemical impedance spectroscopy. These measurements are carried out in simulated acid rain (0.2 g/L $NaNO_3$ + 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ at pH 5) which simulates the rain in urban atmosphere. The surface of modified samples is also examined by scanning electron microscopy and Fourier transform infrared spectroscopy in order to verify adsorption of phosphonic acid on metal and formation of an ordered organic layer.

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Calculation of mechanistic parameters of the oxygen evolution reaction

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Energy is the most important issue of the 21st century. With the increase of worldwide energy demands, sustainable energy resources are in focus more than ever. In addition to currently existing intermittent energy sources, efficient energy conversion and storage systems are required. Electrochemical water splitting is one of the promising approaches to contain excess of energy in form of hydrogen. However, the efficiency is limited by the sluggish kinetics of anodic half-cell reaction, viz., oxygen evolution reaction (OER, $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$). To overcome this limitation, researchers have examined a number of strategies to develop more active OER catalysts. However, despite numerous studies devoted to OER, the mechanism of OER on transition metal oxides remains controversial.

There are several mechanistic schemes proposed by different scientific groups since the 1960's. We classified them into three prototypical mechanism recently [1]. First, the most commonly discussed mechanisms emphasize the acid-base chemistry of the adsorbates with little change of the metal valence. Second, mechanisms have been proposed where a high metal valence must be achieved for breaking of the oxygen bond, which is known for oxygen evolution by natural photosynthesis. We have previously compared the mechanism of $LiMn_2O_4$ to that of photosystem II (PSII) under the assumption that the latter was an electrocatalytic surface [2], which provides a link to commonly studies oxides. Thirdly, mechanisms gained renewed interest recently where oxygen comes from the crystal lattice rather than adsorbed water/hydroxide. It is currently unknown how these prototypical mechanisms can be distinguished best. We calculated the Tafel slopes for these cases based on microkinetic analysis. We assumed OH-covered metal sites as resting state, which is more likely in alkaline solution. This contrasts previous similar analyses [3] based on bare metal sites. This information will guide the design of in situ experiments to experimentally identify one of the prototypical mechanisms on an oxide catalyst. A deeper understanding of the mechanism is desperately needed as it opens the ability to improve the mechanism and thereby enhance the activity beyond the present limitations.

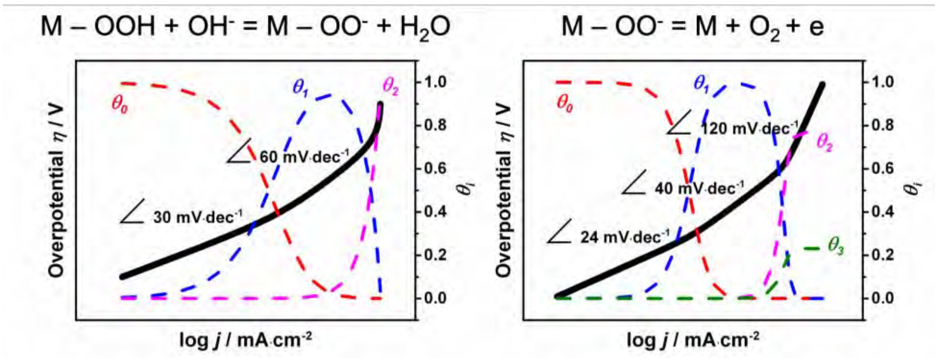

Fig.1.Tafel slope simulations of the two mainly discussed rate-limiting steps of the adsorption mechanism.

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Development and upscaling of gas diffusion electrodes for CO_2 reduction and electrosynthesis of chemicals

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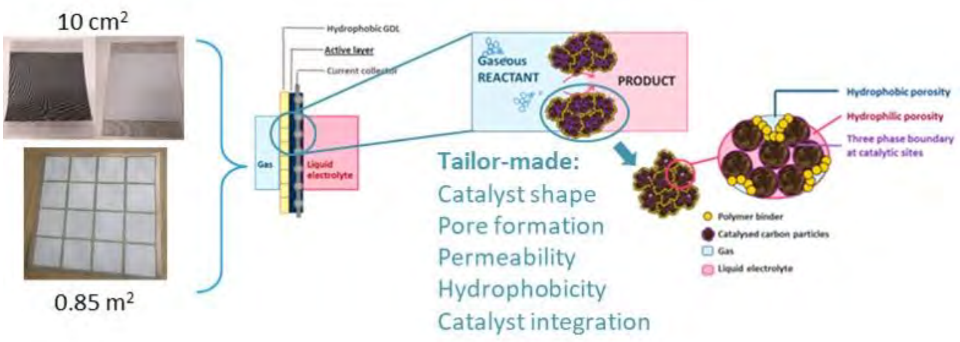
Technologies related to gas diffusion electrodes (GDEs) offer solutions for gaseous reagents taking part in electrochemical reactions. (Bio)electrochemical processes suffer from challenges like high costs of platinized electrodes[1]; rapid catalyst degradation and low performance due to non-uniform electrode quality[2]; difficulties in upscaling. Scaling up microbial fuel cells (MFCs) requires use of large electrodes which are often difficult to fabricate without loss in quality. VITO has developed GDEs tailored for systems with aqueous electrolytes and a gas-water interface, which are characterized by controllable pore diameters in the polymer-bound active layer, mechanical robustness and low water permeability[2]. These cold-rolled (VITOCORE®) and phase-inversion based (VITO CASE®) electrodes enable reproducible quality in sizes from 10 cm^2 to 1 m^2. Large-scale VITOCORE® air cathodes were recently developed and tested in 85 L and 255 L MFCs to evaluate the impact of the cathode size on MFC performance[4,5]. For CO_2 electroreduction, GDEs based on Sn, Cu and Pd were developed and evaluated for production of formic acid and oxalic acid.



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Search for Organic Molecules for Use in Redox Flow Batteries

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Nowadays, large fraction of energy generation is from renewable sources; however, due to their intermittent behavior, it is impossible to make use of them whenever more energy is needed. Therefore, it is important to store large amount of the produced energy for use when the demand for energy is high. Redox flow batteries (RFBs) are a well-suitable choice to store energy but their current cost is too high, and commercialized systems require critical raw materials such as vanadium [1-3]. Our aim is to look for alternative materials for flow batteries. For this purpose, in our research we are looking for new organic molecules that can be used in aqueous RFBs. Although molecule screenings like this has been done before, in our work we evaluated over 20 commercially available organic molecules for flow battery applications that most of them were not studied before for the purpose of using in RFBs. These compounds were selected based on their commercial availability and based on their chemical structures that indicate redox activity because of their functional groups. The best possible candidates for use in RFBs were chosen according to their redox behavior, solubility and stability. Carminic acid, Gallocyanine, Indigo Carmine, Methylene Blue, Neutral Red, O-Dianisidine, Promethazine hydrochloride, Safranin O, Toluidine Blue O, H_2TauNDI (N, N'-di(ethanesulfonic acid)-1,4,5,8-naphthalenediimide) were the ones with promising results so that they can be tested for use in RFBs. Cyclic voltammetry (CV) measurements were done to determine redox behavior and stability of compounds. Concentration of 1mM of the solute and three different solvents such as 0.5M Sulfuric acid, 0.5M Potassium Sulfate and 100mM Sodium Hydroxide was used for pH 1,7 and 13 respectively. During the first scans, the full potential range was examined, and appropriate parameters were selected based on the redox peaks present, then scanning was repeated with different scan rates. According to the results, aforementioned molecules shows reversible reaction peak in acidic solution expect Carminic acid and H_2TauNDI. Standard redox potential of these molecules based on their CV result at scan rate 10mV/s, is shown in Figure 1.

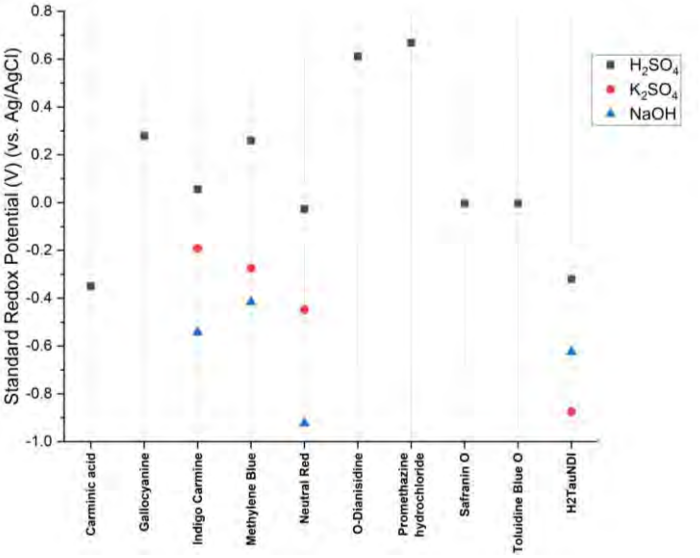

Figure 1- Standard redox potential of promising candidates, sweep rate 10mV/s

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Fermented whey as natural descaling agent: Electrochemical and microscopical analysis

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The characterization of fouling and corrosion of steel is relevant to many industries including oil and gas, automotive, construction and home appliances. Electrochemical characterization of fouling and corrosion is rapid and effective, allowing routine analysis under a broad range of environmental conditions. Tap water in Nur-Sultan, Kazakhstan, is rich in carbonate due to contamination of surface water and insufficient drinking water treatment. This leads to strong fouling and corrosion-related problems in both home appliances and water transportation infrastructure. A broad range of de-scaling agents is available for industrial applications. However, access to chemical and services is still a major problem in rural Kazakhstan community, thus traditional methods are still used, which employ locally available materials. In the rural communities of the south-west regions, de-scaling of cooking equipment is carried out by fermented whey, which is widely available as by product of small-scale faming activities, and is rich in lactic acid, with a low pH ~ 2.8. The de-scaling properties of lactic acid are well-known, thus it is possible to formulate a low-cost, environmental friendly de-scaling agent for use in rural communities.

In this work, the scaling process of mild steel coupons was carried out through carbonate precipitation, which were then cleaned with water, fermented whey and food-grade vinegar as control (pH ~ 3). The scaling and de-scaling process were characterized through electrochemical methods and scanning electron microscopy (SEM). While the traditional cleaning time was ~ 15 h, it was observed that 3 h of treatment are sufficient for the de-scaling process. The corrosion potential and the corrosion current decrease after formation of the carbonate deposit (Figure 1). While both application of fermented whey and vinegar remove the fouling layer, they cause substantial pitting corrosion (Figure 1). A corrosion inhibitor should be added to prevent this effect. Overall, these results show that fermented whey can be used as environmentally friendly de-scaling agent. However, the traditional method of application causes damage to the steel surface and must be optimized, decreasing the exposure time and adding an inorganic corrosion inhibitor.

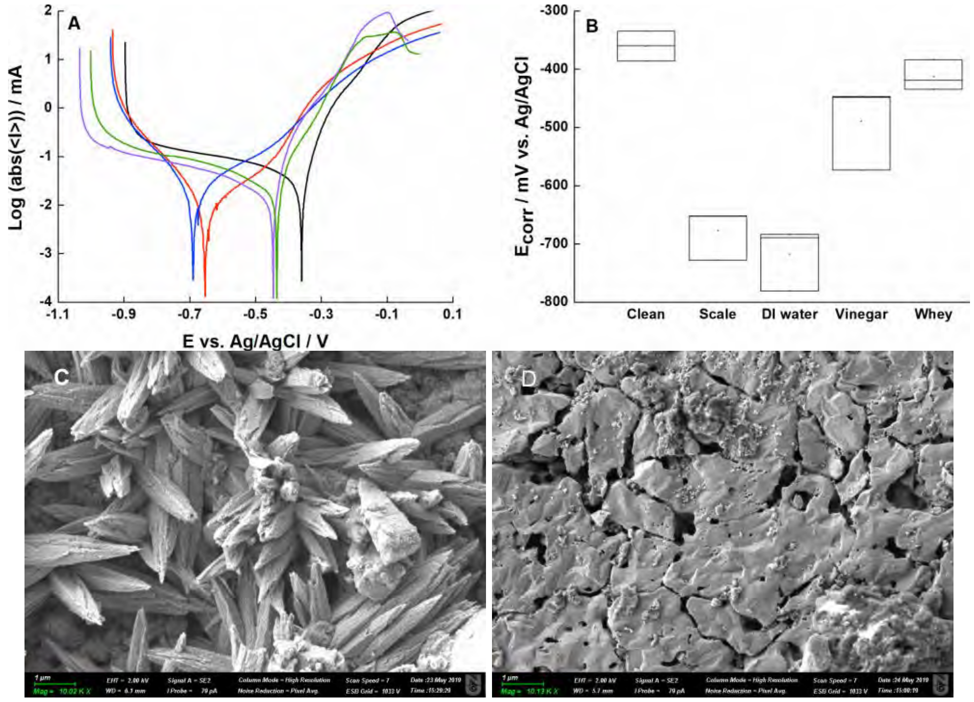

Figure 1: (A) Linear Sweep Voltammetry of mild steel coupons before (black) and after carbonate fouling (red), after cleaning with distilled water (blue), vinegar (magenta) and fermented whey (green); (B) Corrosion potential; SEM of (C) Scaled mild steel coupon; (D) whey cleaned.

Recurrence Quantification Analysis as a Tool to Investigate Current Oscillations Observed During the Mass-Transport Controlled Electrodissolution of Fe in Sulfuric Acid Solutions

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Recurrence is a fundamental property of nonlinear dynamical systems, which can be utilized in order to characterize the system dynamics in phase space. A visual tool for exploiting the recurrence behavior of phase space trajectories is the recurrence plot (RP) introduced in 1987 by Eckman et al [1]. On the basis of the RP, recurrence quantification analysis (RQA) can be carried out to identify different dynamical regimes and characterize transitions between them. Recurrence plots (RPs) and recurrence quantification analysis have been widely used in many scientific fields from chemistry, physics and engineering to life sciences, ecology and economy [2, 3]. RQA was also turned out to be a key issue revealing complex dynamics, phase and generalized synchronization in non-phase-coherent and even non-stationary time series of electrochemical systems and characterizing different corrosion states of metals and alloys [4-6]. This study aims in exploring non-linear quantifiers based on RPs and RQA in order to investigate complex current oscillations observed during the mass-transport controlled electrodissolution of iron in sulfuric acid solutions (Fe|0.75 M H_2SO_4 interfacial system). Under the potentiodynamic operation mode, Fe|0.75 M H_2SO_4 is a well-known electrochemical system exhibiting multiple oscillatory potential regimes depending on various control parameters [7]. Our focus here is on oscillations appeared in the limiting current region beyond a critical value of the ohmic potential drop and when proper hydrodynamic conditions are established across the interfacial region [8]. By applying two system configurations comprising an upward and a downward-facing Fe-disc electrode, visual changes in RPs plots and RQA measures, such as the average diagonal line (ADL), the trapping time (TT) and the longest vertical line (LVL) along with a new entropy quantifier, reveal different nonlinear correlations. The new entropy quantifier was based on recurrence matrix microstates that represent more general properties of the recurrence space as compared with the entropy quantifier based on just diagonal or horizontal lines of the recurrence space [9]. Indeed, the microstate-based entropy quantifier reflects correctly the system complexity in agreement with ADL, TT and LVL. All RQA measures indicate that the enhancement of the mass transfer affects the complexity and the transitions between different nonlinear dynamical regimes.

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Doped-MnO_2 Nano-Electrocatalysts for the ORR in Non-Aqueous Solvents

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Due to the remarkably high theoretical energy and light weight, metal-air batteries represent one class of promising power sources for applications in next-generation electronics, electrified transportation and energy storage of smart grids [1]. The most prominent feature of a metal-air battery is the combination of a metal anode with high energy density and an air electrode with open structure to draw cathode active materials (*i.e.* oxygen) from air [1]. Gas Diffusion Electrodes (GDEs), made of a two-layer or a three-layer structure, are widely used as cathode in metal-air devices [3]. However, one of the main drawbacks related to the cathodic reaction (ORR) is the overpotential loss (about 0.3-0.4 V) under operation condition. Thus, lots of efforts were spent to inhibit the voltage loss requiring an effective ORR catalyst [1,4]. One of the most promising materials, in terms of both performances and costs, seems to be manganese dioxide. According to the recent literature, MnO_2 would ensure capacities comparable to those of platinum, letting higher capacity retention to be reached in non-aqueous electrolytes to prevent Li decomposition [5,6].

In the present work, the electrochemical performances of either bare or Fe/Co-doped (at both 2% and 5%) MnO_2 nano-electrocatalysts are evaluated by Linear Sweep Voltammetries (LSVs). The crystal structure and the surface properties of the present materials are examined by means of XRPD, BET-BJH, TEM, SEM/EDX and XPS analyses. Correlations between their physico-chemical features and the final electrocatalytic performances are drawn. Experimental results reveal that the as-synthesized powders have excellent electrochemical properties in organic electrolytes (0.15 M $LiNO_3$ in propylene carbonate, PC) showing a shift of the onset potential of about 150 mV with 2% Co-doped MnO_2 (Figure 1), thus resulting very promising candidates to be used in lithium-air batteries.

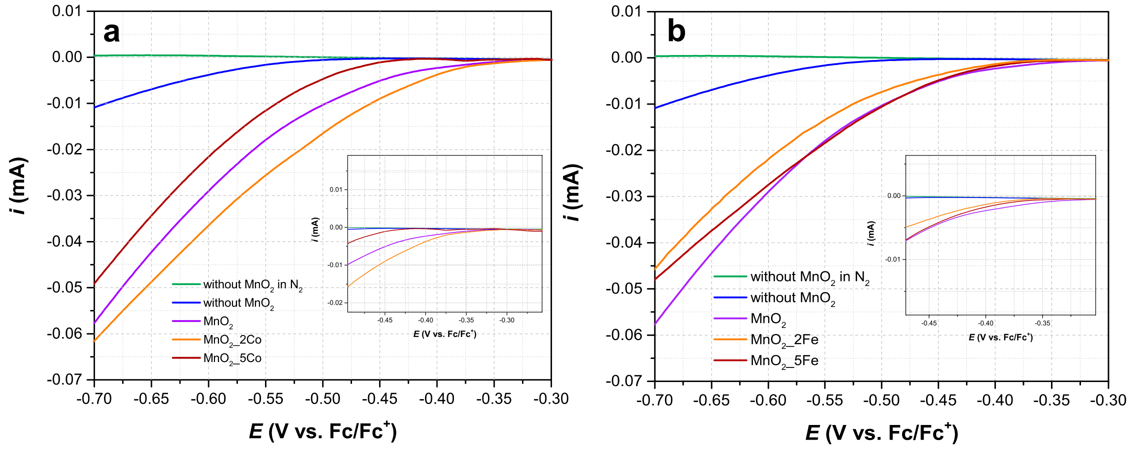

Figure 1. Comparison of ORR onset potentials obtained with (a) Co-doped and (b) Fe-doped MnO_2 nano-electrocatalysts modified glassy carbon electrodes through LSVs tests (in 0.15 M $LiNO_3$/PC).

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Platinum black- and Prussian blue-modified microelectrodes for biomedically relevant hydrogen peroxide detection

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Next to the free radical superoxide ($O_2^{-}\cdot$) and hydroxyl radical ($OH\cdot$), the stable and non-radical hydrogen peroxide (H_2O_2) is one of the most extensively studied reactive oxygen species (ROS). This group of destructive molecules can lead to protein oxidation, lipid peroxidation, and DNA damage and elevated ROS production leads to oxidative stress. Therefore, its detection is of particular interest since the involvement and concentration levels of H_2O_2 at the cellular level are not fully understood yet. H_2O_2 is frequently determined via electrochemical measurements. However, the relatively high oxidation potential (+0.6 V vs. Ag/AgCl) of H_2O_2 may lead to false positive results due to co-oxidizable compounds such as ascorbic acid, catecholamines etc., present in biomedically relevant samples [1].

To overcome these challenges, strategies for electrochemical H_2O_2 detection at low potential will be presented avoiding such interference problems based on electrocatalytically modified microelectrodes. As these studies are targeted towards cell measurements (granulocytes and peripheral blood mononuclear cells from pigs, which are subjected to an acute subdural hematoma) at low sample volumes, microelectrodes will be used. To enhance sensitivity for H_2O_2 detection, microelectrodes are modified with Platinum black (H_2O_2 detection at +0.3 V vs. Ag/AgCl) [2] or Prussian Blue (PB) (H_2O_2 detection at +0.05 V vs. Ag/AgCl) [3,4]. As catecholamines are administered during the recovery phase of pigs, a two-electrode approach is pursued using Platinum black modified electrode for H_2O_2 detection and for example, a carbon fiber electrode (+0.4 V vs. Ag/AgCl) for the detection of catecholamines. Carbon based electrodes are suitable for the detection of catecholamines such as norepinephrine and epinephrine [5] but show no significant signal for H_2O_2 at the detection potential. Next to the thorough characterization of the microsensors, measurements alongside control experiments at granulocytes and peripheral blood mononuclear cells from pigs, which are subjected to an acute subdural hematoma, will be presented.

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Electrochemical impedance time variation of electrodialysis using lithium ion electrolyte $La_{0.57}Li_{0.29}TiO_3$

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There is a need for a better recovery technology for supplying a large amount of high-purity lithium for a lithium-ion battery at low cost. Electrodialysis using a lithium-ion electrolyte is a promising candidate technology. When electrodialysis was performed using a lithium ion electrolyte $La_{0.57}Li_{0.29}TiO_3$ (LLTO) plate, despite the constant applied voltage, as shown in Figure 1, the lithium transfer rate increased with the dialysis time to a certain value. In this research, we clarify the cause of this peculiar phenomenon.

An anode (primary solution side) and a cathode (secondary solution side) electrodes were formed on both sides of the LLTO. Reference electrodes were formed on the LLTO surfaces away from the anode and cathode. The reference electrodes were placed inside or outside the solution, depending on the experimental purpose. A DC voltage was applied between the anode and the cathode. The electrochemical impedances between the reference electrode on the primary solution side and the anode and between the reference electrode on the secondary solution side and the cathode during the application of this voltage were measured by AC impedance method. The measured electrochemical impedances correspond to the ionic conduction resistance and electrode reaction resistance of the electrolyte near both surfaces of the LLTO.

As shown in Figure 2, all these resistances were stable on the primary side regardless of time, but on the secondary side, they decreased toward constant values during voltage application. The values on the secondary side were greater than those on the primary side.

It is considered that these phenomena are caused by uneven distribution of Li^+ concentration generated in the LLTO plate during electrodialysis. That is, the Li^+ elution reaction into the solution that occurs on the secondary surface of LLTO is slow, and the Li^+ concentration increases near the secondary surface of LLTO during voltage application. At this time, titanium ions are reduced from tetravalent to trivalent for charge compensation. This reduction causes the crystal lattice to expand. As a result, the bottleneck of Li^+ migration widens, and the electrode reaction resistance on the secondary solution side of LLTO and the electrolyte resistance near the surface decrease. These changes stop when equilibrium is reached. The phenomenon shown in Figure 1 may be the result of these series of changes due to the uneven distribution of Li^+.

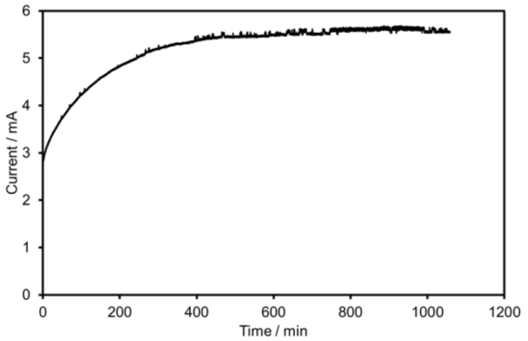

Figure 1 Current change with electrodialysis time.

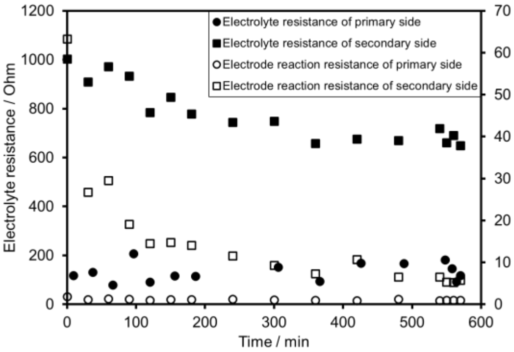

Figure 2 Changes in electrolyte resistance and electrode reaction resistance with electrodialysis time.

n-doped GaP nanowires: Potential Photocatalytic cathodes for Carbon (IV) oxide reduction

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Increasing CO_2 concentration in the atmosphere is believed to have a profound impact on the global climate. One of the ways to reverse this negative impact is developing effective strategies to capture and utilize CO_2 from the atmosphere. Among several available strategies, CO_2 reduction via the electrochemical or photochemical approach is particularly attractive since the required energy input can be potentially supplied from renewable sources such as solar energy [1]

Compared to other available semiconductors, gallium phosphide (GaP) is considered a highly promising photocathode material for solar-fuel conversion. Its high conduction band edge allows it to reduce not only water into hydrogen but also CO_2 into chemical fuels [3]

However, the conventional planar geometry from a single crystalline wafer poses an obstacle to exploring the potential of GaP fully, since in the planar geometry most of the photons absorbed by GaP do not fall within the charge collection layer, as is required for an efficient photo electrode. [3] Recent progress indicates that this issue could be solved when the photo electrode is composed of semiconductor micro wires [4]

We have synthesized GaP nanowires by the reaction between gallium vapor and phosphorus vapor inside a tube furnace system. The as synthesized nanowire Gap were also deposited on carbon nanotubes (CNTs). The nanowires were characterized by Field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). We present some of our findings on the exploration of these nanowires deposited on glassy carbon surfaces and GaP wafers as effective photocathodes for CO_2 reduction.

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Faceting and Nanostructuring of Au through Cathodic Corrosion: Role of Cationic Electrolyte Species and Water

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Gold is one of the most frequently employed electrode materials in electrochemistry due to its exceptional properties such as chemical inertness and high resistance to oxidation and dissolution [1]. According to Pourbaix diagrams, gold is considered stable against degradation under cathodic polarization [2]. In contrast, applying relatively high negative potentials in the presence of alkali metal cations induce notable changes on Au electrode surfaces [3]. In this study, cathodic corrosion of polycrystalline gold in different electrolytes of alkali metal hydroxides has been systemically investigated. In comparison to the recent work [3], this study provides new findings as a function of the applied parameters for the nanostructuring of gold surfaces. Cell design and the distance between the electrodes have carefully been controlled and optimized. The progression of surface restructuring and corrosion features was investigated using cyclic voltammetry (CV) and scanning electron microscopy (SEM). The results show different corrosion features depending on the nature and the concentration of alkali metal hydroxides, on the applied voltage, and on time. Current-potential curves for the modified electrodes in 0.1 M H_2SO_4 show characteristic features in the double-layer and oxidation regions. Cyclic voltamogramms of the corroded electrodes provide evidence about the preferential orientation of facets and the electrochemical active surface area as a function of the applied parameters. SEM micrographs show that polarizing the gold surfaces at relatively high negative potentials generates different size and orientation of octahedral nanocrystals using NaOH, spherical nanoparticles and triangular pits using KOH and triangular pits using LiOH. Besides the alkali metal cations, the electrolyte concentration and the applied voltage are important parameters.

Furthermore, the role of water in cathodic corrosion of gold has been investigated using mixtures of different mole fraction of water and non-aqueous electrolytes. The absence of corrosion features using water-free non-aqueous electrolytes reveal that water plays a key role in the cathodic corrosion process.

In addition, various aqueous mixed electrolytes have been systemically investigated. The results show combined corrosion features according to the mole fraction of different cations. For example, a 1:1 NaOH + LiOH mixture leads to the formation of rectangular pits which are attributed to (100)-facets compared to a 1:1 KOH + LiOH mixture which leads to triangular pits revealing the formation of (111)-facets.

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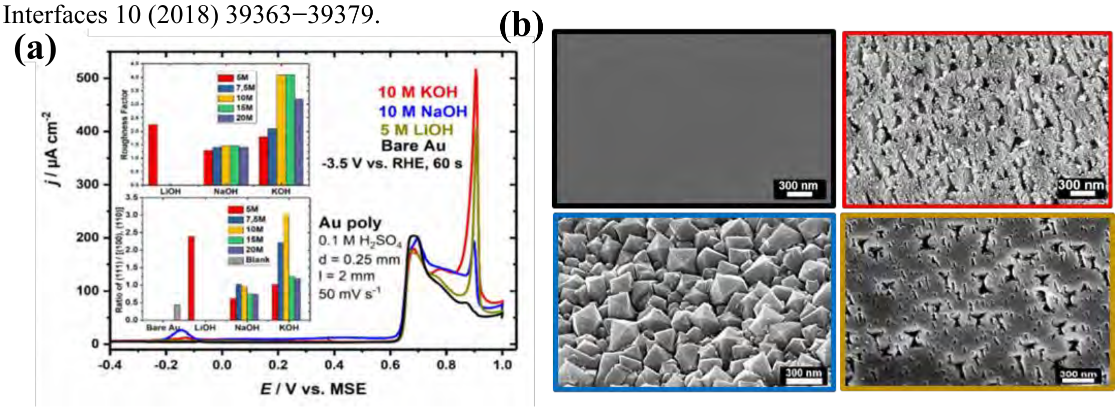

Figure 1. (a) Current density-potential curves for Au after cathodic corrosion in concentrated hydroxide solution at -3.5 V for 60 seconds. Different roughness factors and distribution of facets are shown in the inset. (b) Selected SEM micrographs of gold surfaces before and after cathodic corrosion.

Electrochemical Evaluation of Various Nanoparticles-based Sensors for Levothyroxine Detection

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Carbon-based nanoparticles, such as graphene and carbon nanotubes or gold nanoparticles are widely used since they are good conducting materials, assure an enhanced effective surface area and biocompatibility or are able to catalyze specific reactions.

Levothyroxine (LT4) is used as medication in a large variety of medical conditions, like hypothyroidism, where the best therapy is the hormone replacement. LT4 replaces the thyroxine hormone normally produced by the thyroid gland which regulates the body's energy and metabolism. Since the effect of administration of LT4 can be monitored mainly through clinical observations, monitoring of LT4 levels requires a simple, reliable tool, such as label-free nanoparticle based sensors. Analyzed carbon nanotubes in this work can act similar to enzymes, and thus they have been used for label-free sensors development as rapid screening tools for LT4 with a sensitivity of 4 μA cm^{-2} μM^{-1} and a limit of detection in nanomolar range.

Electrochemistry was used for the characterization, comparison and optimization of the most suitable nanoparticle-based sensors for LT4 detection (Fig. 1). The oxidation mechanisms of LT4 together with the interfacial changes, which occur due to their electrochemical properties at sensor surfaces, were studied by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The analytical performance of the sensors was evaluated by differential pulse voltammetry (DPV).

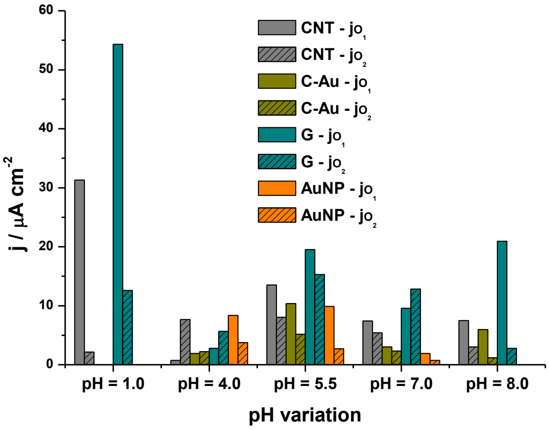

Fig. 1. Histogram representing current densities of the two oxidation peaks O1 and O2 from DPVs in 0.1 M various electrolytesfor carbon nanotubes (CNT), graphene (G), gold nanoparticles (AuNP) and a mixture of CNT-AuNP (C-Au).

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Electrochemical fingerprinting of cathinones and adulterants for their sensitive detection in street samples

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The abuse of illicit drugs has become a global concern considering its close relationship with the increasing incidents of crimes and severe social problems. The widespread use of illicit drugs and the consequences of drug abuse on individuals and societies has led to increasing efforts to quickly and accurately detect drugs on-site. The current methods used to quickly detect drugs on-site are presumptive tests, such as color-tests. However, they lack selectivity, giving a high number of false negative and false positive results, due to the presence of adulterants and cutting agents.

Electrochemical methods proved to be excellent techniques for the fast determination of drugs with high sensitivity and specificity, suitable for the development of miniaturized portable devices to be used in-field.

Drugs are usually adulterated with adulterants (added to modify the properties of the drugs or to mimic the drugs' effects, e.g. procaine has local anesthetic effect similar to cocaine) or diluted with cutting agents (used to 'cut' or 'dilute' the sample). The characterization of cutting agents and adulterants in seized cocaine samples is important from a forensic point of view in order to link different seizures to one original batch, as well as for the health implications some of them might have. For instance, levamisole used as adulterant in cocaine samples was linked to serious adverse effects such as leukoencephalopathy.

We used nanomaterials-modified electrodes to detect cathinones and adulterants/cutting agents by means of square wave voltammetry. We tested several nanomaterials-based platforms and depending on the obtained signal for the oxidation of drugs we chose graphene and carbon-nanotubes based platform to further test cathinones. We investigated several cathinones (such as methcatynone, chloroetcathinone) and adulterants/cutting agents such as mannitol, sorbitol, procaine, benzocaine, creatine. The effectiveness of the developed method was tested for the detection of drugs in simulated drugs samples.

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Electrodeposition of 1D Bismuth Nanostructures Using Deep Eutectic Solvents for Electrochemical Detection

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1D nanostructures exhibit a very high surface to volume ratio as well as unique electrical properties which make them ideal candidates to build high performance electrochemical sensors and bio-sensors [1]. Bismuth nanostructures are considered as “green” electrode materials since 2000 and gained an increased interest for detecting various analytes [2]. Usually, size- and shape-controlled Bi nanowires (Bi NWs) are electrochemically synthesized involving aqueous electrolytes and template-assisted method. Other 1D Bi nanostructures may be prepared using the hydrogen bubble template electrodeposition method [3].

Herein, the electrochemical synthesis of Bi NWs is reported, involving electrolytes based on eutectic mixtures of choline chloride with oxalic acid or malonic acid (the so-called “deep eutectic solvents” – DES). The”soft template” electrodeposition based on a proper selection of the surfactant/stabilizer, as well as the classical template-assisted method using porous membranes have been applied (see Fig.1).

The electrochemically synthesized nanowires have been characterized using SEM, STEM and XRD investigations. Cyclic voltammetry has been selected as electrochemical technique in order to get more information on the Bi NWs deposition process and on the influence of the main operation parameters, mainly the applied current density/deposition potential, and the electrolyte composition. A comparative analysis of the structural features of the obtained Bi NWs using the soft template method and the traditional template-assisted technique is provided, too.

In addition, preliminary results related to their electrochemical sensing performance for folic acid and hydrogen peroxide are also discussed.

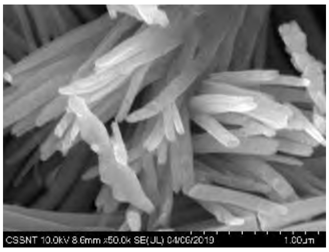

Figure 1. SEM micrograph of Bi NWs using „soft” template

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Electrochemical fingerprints of cocaine and cathinones on nanomaterials

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Illicit drugs use and abuse remains an increasing challenge for worldwide authorities and, therefore, it is important to have accurate methods to detect them in seized samples, biological fluids and wastewaters. They are recently classified as the latest group of emerging pollutants as their consumption increased tremendously in recent years.

Nanomaterials have gained much attention over the last decade in the development of sensors for a myriad of applications. The applicability of these nanomaterials, functionalized or not, significantly increases and are therefore highly suitable for use in the detection of drugs of abuse.

We have assessed the suitability of various nanoplatforms for the electrochemical detection of illicit drugs, such as graphene, singled-walled carbon nanotubes, multi-walled carbon nanotubes functionalized with platinum nanoparticles, gold nanoparticles and platinum nanoparticles. Graphene and singled-walled carbon nanotubes were drop-casted onto graphite screen printed electrodes and left to dry at room temperature. Multi-walled carbon nanotubes were functionalized with platinum nanoparticles using a simple and efficient chemical process, in which carboxylic acid-functionalized multi-walled carbon nanotubes were mixed with chloroplatinic acid in a mixture of ethylene glycol and water to result in platinum-functionalized multi-walled carbon nanotubes. The functionalized multiwalled carbon nanotubes were drop-casted onto graphite screen printed electrodes. Gold and platinum nanoparticles were deposited by electrodeposition from a solution of chloroauric acid and chloroplatinic acid, respectively, by cyclic voltammetry.

The electrochemical fingerprints of cocaine and cathinones (such as mephedrone, alpha-polyvinylpirolidone, methylmethcatinone, chloroethcatinone, chloromethcathinone, etylone) were elucidated on the above-mentioned nanoplatforms. Square wave voltammetry was performed as a high-performance electrochemical method. This allowed for the sensitive and selective (class selectivity) of the investigated illicit drugs.

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Ceramic Nanofibers: A versatile material class to improve Electrochemical Energy Applications

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Nanofibers exhibit a large surface-to-volume ratio as well as high porosity. Ceramic materials have excellent thermal stability and are largely chemically inert.[1] In electrochemical energy devices, such as fuel cells, electrolyzers and batteries, (electro-) chemical reactions take place at the interface of an electrode with gas (H_2/O_2), a liquid or an electrolyte, respectively. In these devices, the combination of a high active surface area for improved reaction rates, large porosity for a substantial material flux, thermal and chemical stability for long term operation as well as conductivity for electron transport processes are of vital interest. Nanofibers are usually fabricated by the electrospinning technique. The liaison of appropriate material combinations, spinning parameters and post-treatment procedures gives rise to a vast spectrum of tailored nanofibers with fine-tuned properties such as catalytic activity, electrical conductivity, radical scavenging activity or chemical resistance.[2]

In our work, we demonstrate with two recent examples, that the integration of ceramic nanofibers into electrochemical energy systems enables significant improvement of the properties of electrochemical enery systems: In Fig. 1 (left) CeO_2 nanofibers are shown, which can be used as radical scavenging membrane additive. Secondly, IrOx nanofibers enable a significant reduction of - usually expensive - catalytic material *via* providing electrically conductive pathways (Fig. 1, right). Upon reducing the amount of catalytic material, islands of non-connected catalyst are formed. Conductive ceramic nanofibers electrically link these islands, thus utilizing more catalytically active surface area. By this approach, we showed a reduction of 80% Iridium oxide at the anode of a proton exchange membrane (PEM) water electrolyzer cell while maintaining its high performance.[3]

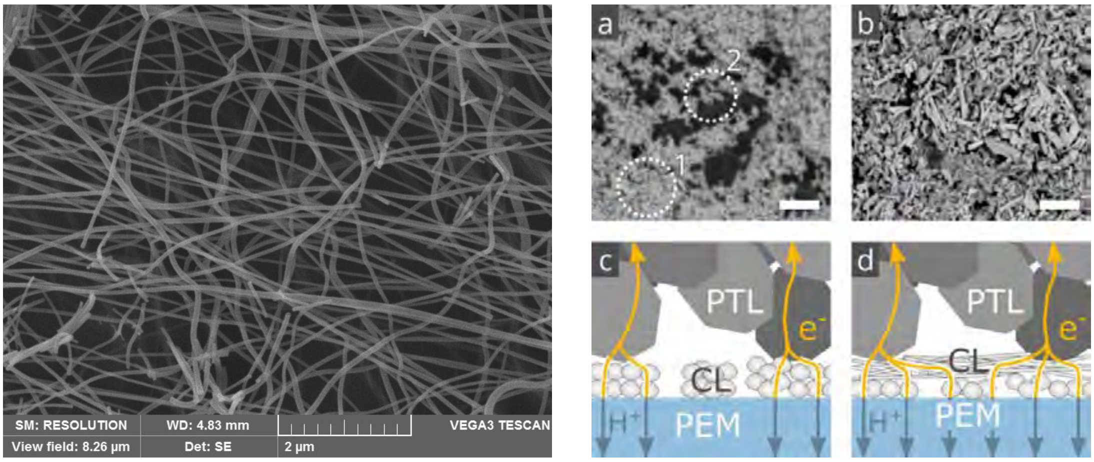

Figure 1. left: Cerium oxide nanofibers as radical scavenger for PEM fuel cells, right: Iridium oxide nanofibers connecting isolated catalyst islands.

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Stabilization effect of Pt on FeNC: A gateway to elucidation of degradation mechanism of FeNC in PEMFC

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Hydrogen fuel cells (such as PEMFC) could reduce or possibly replace the fossil fuel dependency if the high cost and low durability issues of the fuel cells are resolved. Non-precious metal-based materials (such as FeNC) are promising candidates to replace expensive Pt-based catalysts and thereby reducing the cost of the fuel cells. Although these catalysts show a decent activity, their poor stability, especially at high potentials, limits their applicability.[1,2]

Among the various approaches to stabilize FeNC catalyst, our recent approach of adding minute amount (0.5-2 wt%) of Pt was successful in stabilizing FeNC. Pt itself remains in an ORR-inactive state throughout the measurement.[3] Although stabilization with the addition of Pt, which itself is an expensive metal, may not be a better option, a proper illustration of how Pt stabilizes FeNC during ORR in fuel cell would give us a better insight into the degradation mechanism of FeNC.

Here, we elucidate the nature of this Pt-species and its role in the stabilization of the Fe-N-C to understand FeNC degradation mechanism and possible ways to prevent them. Structural analysis with high-resolution TEM of the hybrid Pt/Fe-N-C catalyst, indicate a protective Fe-shell is formed around the Pt-particles, making them ORR-inactive. Nevertheless, electrochemical analysis proves that the hybrid catalyst reduces H_2O_2 formation (an undesirable side product of ORR) as well as reduced catalyst degradation. Besides, electron paramagnetic resonance (EPR) spectroscopy on hybrid Pt/Fe-N-C shows the formation of less radical oxygen species (ROS), which are potentially harmful to the catalyst (Figure 1). These results prove the ability of the deposited Pt-species to significantly reduce the amount of ROS, ultimately increasing the stability of hybrid Pt/Fe-N-C in PEMFC.

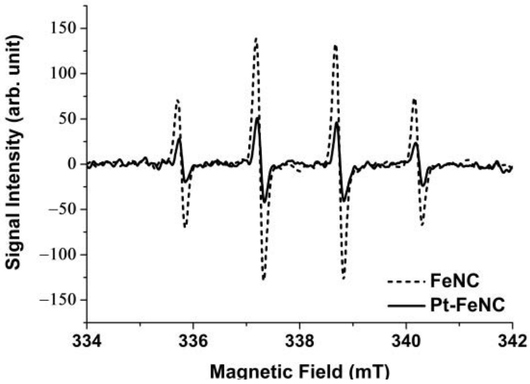

Figure 1: X-band EPR spectra recorded at 298 K of DMPO/•OH spin adduct generated during H_2O_2 treatment of FeNC (dashed line) and Pt-FeNC (solid line) in presence of DMPO spin trap.

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Automated Image Analysis for Supported Nanoparticulate Electrocatalyst Characterization

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In order to tackle the environmental issues, caused by our excessive reliance on fossil fuels, one of the things we need to develop are efficient alternatives to internal combustion engines for transportation. One alternative are low-temperature proton exchange membrane (PEM) fuel cells. To produce clean electricity, PEM fuel cells require an electrocatalyst that is usually based on Pt or Pt-alloy nanoparticles supported on high surface area carbons.

In order to study the structure-activity and structure-stability relations of such materials, transmission electron microscope (TEM) is one of the essential tools commonly used to do so. As part of TEM analysis, numerous microscopic images (in other words large amounts of data) of the studied materials must be taken and analyzed.

To quantify the data within the TEM images, different software options are available [1]. However, most software solutions cannot reliably recognize all the relevant features in an image, such as overlapping and out-of-focus features. For a given type of material, it often turns out that researchers write their own software which is more reliable than the one-size-fits-all commercial options, but the exact code is commonly not made available to the public [2].

In this contribution, we will present new image-analyzing algorithms, which have the potential to be more efficient and reliable than the classical ways of analyzing STEM images. Here, various machine learning methods are included, where the goal is to analyze large amounts of information in a short time and care is taken that the user interaction is kept to a minimum, which will ensure less biased output information [3].

As the studied system, a series of HAADF-STEM images of a platinum-based electrocatalyst were selected, which are in the form of platinum-copper alloy nanoparticles, embedded in a carbon support [4]. The output information includes all the quantifiable data that can be extracted from the images, such as the histograms of size distribution, information about homogeneous surface coverage, spatial information and more. As part of this work, we will discuss how to prepare the input data for analysis, how to obtain output data with novel computational methods and how to deal with challenges such as resolving overlapping particles.

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Influence of Inorganic Acids during Precipitation on Stabilization of Poly(acrylic acid) coated Silver Nanoparticles

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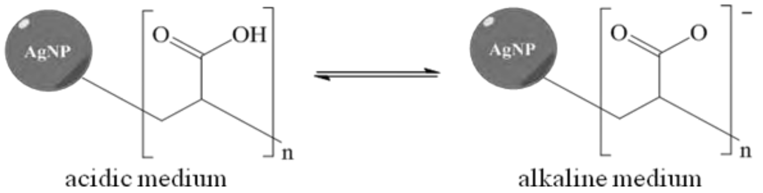
In recent years, silver nanoparticles (AgNPs) have received great attention due to their unique optoelectronic and physicochemical properties resulting in various applications [1, 2]. This study reports a wet chemical synthesis of AgNPs, using hydrazine monohydrate as a reducing agent and poly(acrylic acid) (PAA) as a capping agent [3]. PAA-coated silver nanopowders, precipitated with inorganic acids (perchloric, phosphorous and sulfuric), were used for nano-ink formulations. Characterization of the reaction mixture, as well as of the prepared conductive inks, was performed by cyclic voltammetry and UV-Vis spectroscopy, respectively.



Schematic presentation of PAA-encapsulated AgNPs in acidic and alkaline medium.

PAA adsorbed on the nanoparticle surface behaves as a weak acid. In alkaline media, negative surface charge generated due to the dissociated PAA engenders repulsion forces between nanoparticles. Thus, efficiency of electrostatic stabilization of the prepared suspension depends on the acid dissociation rate. The stability of the formulated nano-inks was tested in a wide range of Britton-Robinson buffer solutions. The highest anodic current responses and maximum absorbance (λ = 419 nm) were plotted versus pH to determine the quantity of surface bound PAA.

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Folded V_2O_5 Scaffolds for High Energy Density Aluminum-Ion Batteries

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Unidirectional ice-templating of aqueous V_2O_5 nanofiber dispersions yielded scaffolds with an anisotropic structure, wherein well-aligned lamellas form ordered channels (**Figure 1a**). The latter are optimally suited to facilitate ion diffusion throughout the entire scaffold architecture. The micrometer-sized pores in the form of cavities as well as the mesoporosity (~5 nm pore size) of the lamellas and pillars lead to an exceptionally high porosity of 99.9% and a high specific surface area of 211 m²/g. By compressing the scaffolds, compact electrodes were obtained. To ensure their mechanical stability, the scaffolds were tested under compression and the microstructure of the resulting compact electrodes was investigated. From the compressive stress-strain curves we concluded that above 50% strain the scaffolds start to densify forming a densely packed disc at 80% strain. The latter shows a two-fold enhancement of the electrical conductivity vs. the pristine sample. Microstructural analysis of the densely packed disc evidenced the presence of an open surface porosity, as well as a corrugated lamella structure that comprises new contact points (**Figure 1b)**. The preservation of a high porosity (99.6%) and the transformation into a folded lamella structure without any appreciable damage represent exceptional features of these scaffolds, appointing them as outstanding in respect to other cathode materials. The extraordinary anisotropic porosity of the electrodes, combined with their large surface area, effectively compensate for the restricted diffusion of the ions, thus allowing for the discharging of the cathodes at higher current densities (500 mA/g, 105 mAh/g vs. 2000 mA/g, 58 mAh/g) [1]. Moreover, in comparison to the dense paper-like cathode materials, higher capacities at the same current density were achieved, which further highlights the importance of the unique porous structure. The increased area of the electrode/electrolyte interface and the channel-like structure along the ion diffusion paths (**Figure 1c**) synergistically enable the increase of the applied current densities, while largely preserving the capacity. Remarkably, the porous scaffolds feature significantly increased energy densities up to 52 Wh kg^{-1}, which outperform not only the paper-like cathodes[2], but also the state-of-the-art V_2O_5-based electrodes for aluminum-ion batteries (**Figure 1d**). The developed nanostructured cathodes are promising for application as binder-free electrodes in metal-ion batteries, featuring enhanced capacity and energy density at high current densities.

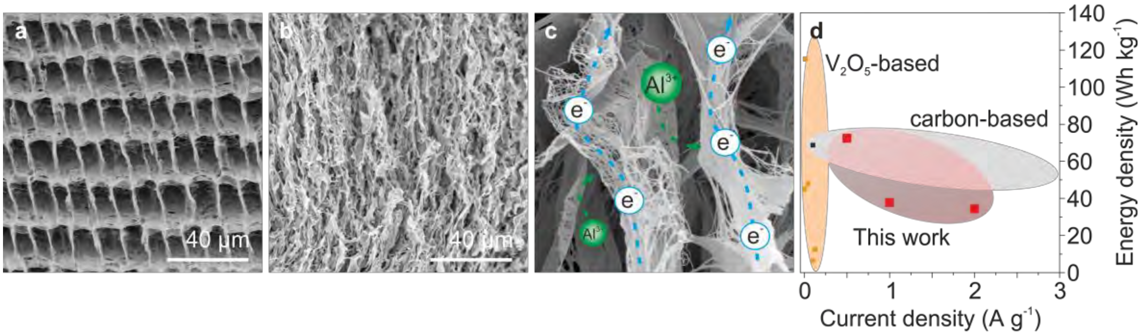

Figure 1. SEM images of the V_2O_5 scaffold microstructure, showing the cross-section and surface (a) before and (b) after compression at 80% strain, respectively. (c) Higher magnification SEM image of the microstructure with characteristic folded lamellas. Overlaid is a schematic illustration of the electron and ion paths during electrochemical cycling. (d) Comparison of the electrochemical performance to state-of-the-art V_2O_5- and carbon-based cathodes.

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Mesoporous Highly Flexible and Biodegradable Cellulose Aerogels as Battery Separators

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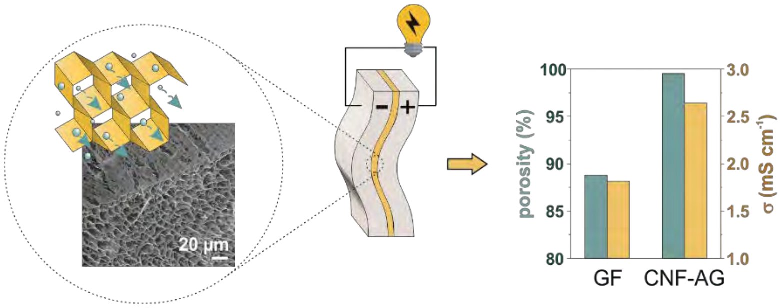

CNF-AG as highly flexible, high performance separator for shape-conformable metal ion batteries.

Flexible separators with minimal impact on the battery cell performance, are nowadays important due to the rapidly developing flexible electronics. In this context, a novel bio-degradable and highly flexible cellulose-nanofiber aerogel (CNF-AG) separator is developed, fabricated by ice-templating. [1], [2] The tailored channel-like structure provides a network of meso- and macropores, yielding a high porosity of 99.5%. The synergy of the high structured porosity, affinity of the cellulose to the electrolytes and mechanical stability greatly improves the separator performance, compared to the state-of-the-art glass fiber (GF) membranes. An enhanced electrolyte uptake capability is obtained, one order of magnitude higher than that for the GF. In addition, the thermal characteristics analysis revealed a high stability up to 200°C, ensuring the separator's suitability for batteries working under harsh conditions. Furthermore, an enhanced ionic conductivity of 2.4 mS cm^{-1} and 8.4 mS cm^{-1} is achieved for Li- and Al-based electrolytes, respectively. The comparison of the Li^+ diffusion coefficient in GF and CNF-AG, revealed 60% faster diffusion in the CNF-AG. Compared to GF, an improved electrochemical performance is obtained, in regards of a decreased interfacial resistance of 300 Ω, and the significantly stable cell cycling ability reaching high specific capacities. The good mechanical stability as well as the low impact on the battery cell performance revealed the suitability of the CNF-AG as separators for metal ion batteries.

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Inherently Chiral Artificial Membranes as Key Components in Chiral Potentiometric Sensors

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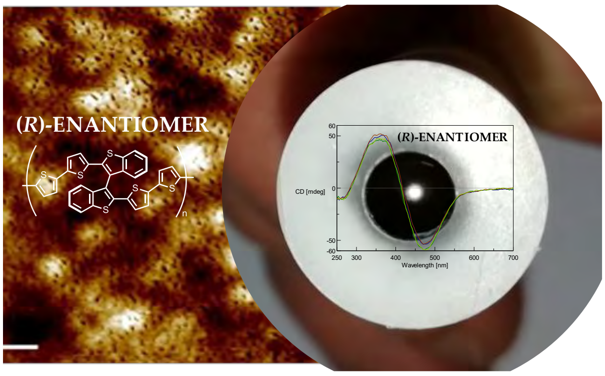
Chiral membranes are important tools for enantiomer discrimination or/and separation in a broad range of applications, especially concerning preparative separations in the pharmaceutic field. Many chiral membranes are of natural origin (*e.g.* polysaccharides, polyaminoacid derivatives), or based on natural chiral components while less common so far are membranes based on synthetic chiral components (*e.g.* calixarenes or crown ethers). However, synthetic chiral membranes have interesting intrinsic features, like wide range of molecular designs and functional properties, equal availability of both enantiomers, and easy synthesis scalability. Among analytical applications of chiral membranes, a potentially interesting one concerns implementation as key components in chiral potentiometric sensors. Concerning design of synthetic membranes, different stereogenic elements can be considered to endow them with chirality, the most common ones being localized stereocenters, but it was observed that much better enantioselection performances can be obtained by implementation of the "inherent chirality" strategy. [1-2] In this frame we have discovered that the electrooligomerization, in acetonitrile as solvent, for 108 deposition cycles, on an ITO electrode support, of our "inherently chiral" benchmark monomer, leads to self-standing racemic or enantiopure membranes. These ones were obtained by simply peeling off the solid deposit from the ITO immersed in water after the electrodeposition in acetonitrile. We have then characterized inherently chiral membranes with different techniques (*e.g* FTIR, HR LDI, scanning electron microscopy, BET for surface area and pore size distribution, CD spectra to check that chirality was fully transferred from the monomer to the oligomer films, and atomic force microscopy) comparing the racemic *vs* enantiopure deposit properties. We have decided to implement enantiopure inherently chiral membranes in a "ion-selective like" set-up in order to study their enantiorecognition capability (as depicted in the Figure). First of all we have verified the potential difference was read correctly through the membrane to allow correct determinations of transmembrane potentials. After that we have tested enantiopure membranes in the presence of chiral charged species (in all configurations for both membranes and internal/external electrode solutions) for determining their enantioselective capability [3]. Preliminary results are very promising and encourage us to perform the scaling up of the membrane electrosynthesis to be used for industrial scopes and to extend the study to other probe useful in the analytical and pharmaceutical field.



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Electrocatalytic Conversion of Bicarbonate Promoted by Surface Hydrophobicity

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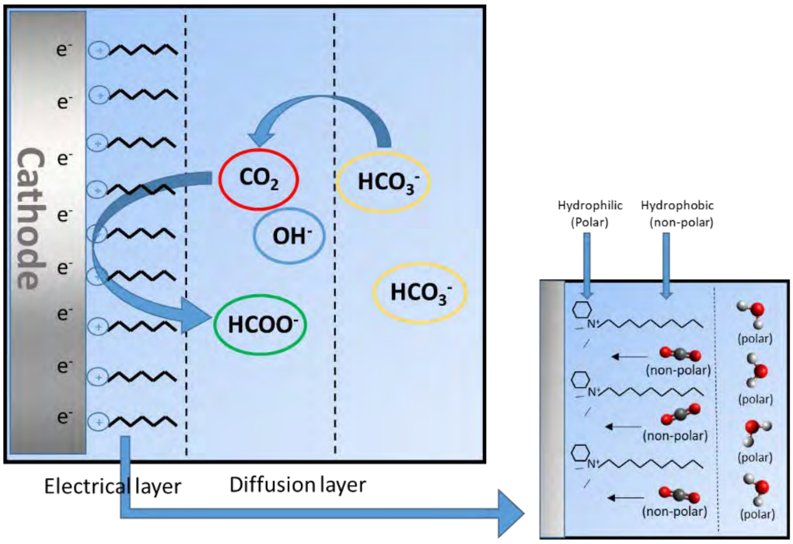
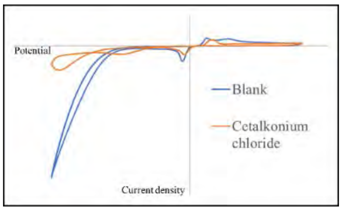
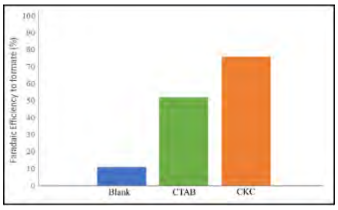
Typical CO_2 electrolyzers require gas feeding or to prior saturate the electrolyte to be able to electrocatalytically convert CO_2 to carbon products. If CO_2 is captured and stored in aqueous alkali solution as a carbon pool, then it can be used as a feedstock for a CO_2 electrolyzer. In weak alkali media, CO_2 is present as bicarbonate (HCO_3^-) and, since it requires high thermal energy to extract the CO_2 back, it is convenient to find an active catalyst and an optimal electrochemical cell able to electrocatalytically convert bicarbonate directly to carbon products. Firsts electrolysis experiments using different concentrations of bicarbonate as carbon source showed faradaic efficiencies around 10% towards formate ($HCOO^-$) at -0,7 V vs RHE using bulk Sn as cathode. The faradaic efficiency variations were negligible when increasing the concentration of bicarbonate and, by comparing the results to analogous experiments using saturated CO_2 solutions, where the faradaic efficiency raised up to more than 70%, it is concluded that, even though there is conversion from bicarbonate solutions, the efficiency is very low compared to typical CO_2 saturated electrolytes. A model is proposed (figure 1) in order to increase the faradaic efficiency of the reduction of bicarbonate by approaching the inhibition of the main co-reaction undergoing at the same time, which is consuming most of the current, the hydrogen evolution reaction (HER). HER is inhibited by forming an hydrophobic non-polar layer close to the surface of the working electrode with the addition of cationic surfactants to the electrolyte. The model is tested by measuring the response of the current within a certain potential range in electrolytes with surfactants of different nature. Cetrimonium bromide (CTAB) is chosen as a potential inhibitor obtaining an increase in the faradaic efficiency from 10 to 50% at -0,7 V vs RHE in 2 M bicarbonate and 2.5 mM CTAB electrolyte. After that, the cationic surfactant is optimized in order to not only inhibit HER, but also promote HCO_3^- reduction. A benzyl-functionalized surfactant, cetalkonium chloride (CKC), is used as HER inhibitor and CO_2R promotor obtaining conversion efficiencies up to 80% in the same conditions, higher than CO_2 saturated electrolytes. It is proven that, by increasing the hydrophobicity of the cathode surface, polar molecules, like water, are repelled while non-polar molecules, like CO_2 (derived from the HCO_3^- aqueous equilibrium), are promoted to cross the hydrophobic layer, approach the surface of the electrode and reduce.







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Electrodeposited Polypyrrole/Polyelectrolyte Films for Ammonia Gas Optical Sensing

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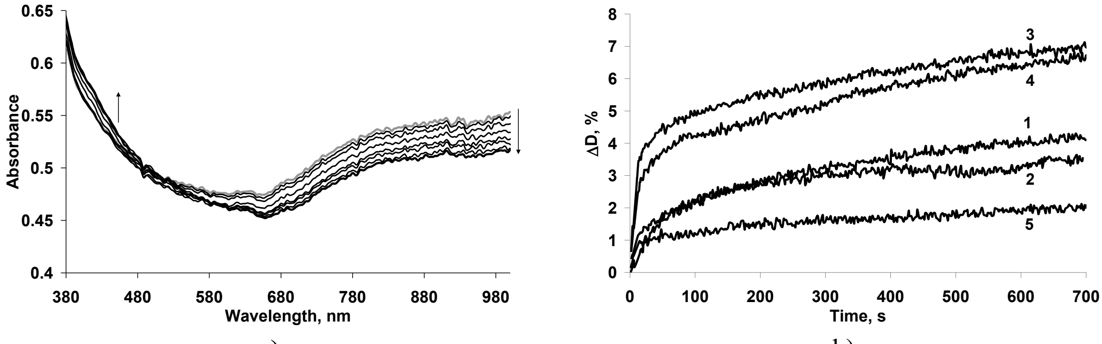
We present a comparative study of pyrrole electrochemical polymerization in aqueous solutions of sulfonated polyelectrolytes with different structure and flexibility of the polymer backbone. Polypyrrole (PPy) synthesis was carried out in the presence of the following polyelectrolytes: flexible-chain poly(styrene-4-sulfonic acid) (PSSA) and poly-2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPSA), semi-rigid-chain poly-(4,4’-(2,2’-disulfoacid)-diphenylen-iso-phthalamide) (i-PASA), rigid-chain poly-(4,4’-(2,2’-disulfoacid)-diphenylen-tere-phthalamide) (t-PASA) and their sodium salts. The processes of PPy electrodeposition in potentiodynamic, potentiostatic and galvanostatic regimes was studied by in situ spectroscopy in the UV-Vis-NIR spectral regions and Raman spectroscopy with simultaneous monitoring of the electrochemical parameters of the synthesis. For comparison, the electrosynthesis of PPy was also carried out in common aqueous solutions of H2SO4 and Na2SO4. The obtained films were characterized by cyclic voltammetry, UV-Vis-NIR spectroelectrochemistry.

It was shown that the course of synthesis and the electronic structure of PPy/polyelectrolyte complexes depended strictly on the structure of polyelectrolyte and the nature of its cation. In the presence of the acid forms of flexible-chain polyelectrolytes the films are formed with higher absorbance in the NIR range (higher degree of charge carriers’ delocalization), with more rough surface and spectroelectrochemical properties similar to those of PPy films obtained in inorganic electrolytes. Contrarily, PPy films obtained in the presence of the acid form of semi-rigid-chain i-PASA are characterized by lesser roughness and lesser degree of charge carriers’ delocalization.

PPy films were successfully tested as sensitive layers in optical ammonia sensors (Fig.1a). The optical responses of these sensors in Vis-NIR spectral range were dependent on the polyelectrolyte structure (Fig.1b). It was shown that optical sensors based on films of PPy complexes with salt forms of all polyelectrolytes and rigid-chain polyelectrolytes in the acid form can detect 25 ppm ammonia with response time about 6 min.



a) b)

Fig.1. Evolution of UV-Vis-NIR absorption spectra of PPy-t-PASA film (a) and responses of PPy films (b) obtained in the presence of PSSA (1), PAMPSA (2), i-PASA (3), t-PASA (4) and H_2SO_4 (5) exposed to 529 ppm NH_3.

The Anode Behavior in Novel Polymer Gel Electrolytes for Secondary Aluminium Batteries

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The production of cheap and sustainable batteries with long lifetime that can compete with Li-ion batteries has been of great interest in recent years. A promising alternative are aluminium batteries, which promise high energy density and low prices.[1] Similar to Li, however, aluminium is prone to dendritic growth ultimately leading to device failure.[2] A promising strategy to circumvent dendritic metal deposition and to enhance battery safety is the use of polymer gel electrolytes. Polyethylene oxide (PEO) as a matrix material has already been studied extensively in Li-ion batteries because it is cheap and shows good electrochemical and thermal stability while maintaining its shape and flexibility.[3,4,5] They can further act as spacer between electrodes without the need of an additional separator.[4] The preparation of polymer gel electrolytes can be done by adding specific amounts of the polymer to the ionic liquid and heating the mixture until the polymer is dissolved. However, it is also possible to add the required monomers directly in the ionic liquid using it as the solvent for polymer synthesis.[6] The presence of a strong native oxide layer present on the aluminium anode also provides a challenge. It is, however, reported in literature that leaving the aluminium anode to soak for a certain amount of time in the electrolyte has a positive effect on the electrochemical performance of the electrode.[7]

We measured the conductivities of the DES and the polymer electrolytes with electrochemical impedance spectroscopy. The deposition/dissolution characteristics of the aluminium anode was tested by galvanostatic cycling in PEO based gel electrolytes with a $AlCl_3$:urea deep eutectic solvent (DES).[8] The mere DES was tested as well as mixtures with different ratios of PEO (1-5 wt%). The experiments were carried out in symmetrical aluminium half-cells and the surface morphologies of the aluminium anodes were studied with SEM/EDS. The soaking time of the aluminium anode in $AlCl_3$:urea DES was optimized to improve the morphology of the deposited aluminium during galvanostatic cycling. The soaking tests were also performed with the polymer electrolytes after finding the optimum with the pure $AlCl_3$:urea deep eutectic. Since the loading of the cells with the viscous polymer electrolytes introduced gas bubbles, a method to remove those and improve the electrode/electrolyte contact was sought. This could be achieved by heating the assembled cells with the PEO based electrolytes to 60°C (melting point of polymer).[9] Further, the impact of this heating step on the overpotentials and the final anode morphology was examined showing good correlations.

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Enhancing the CO-Tolerance of Hydrogen Oxidation Electrocatalysts using Tungsten Oxide: Mechanistic Insights from Spectroelectrochemistry

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The tolerance of hydrogen oxidation electrocatalysts towards fuel contaminants such as carbon monoxide is an important figure of merit in assessing their viability for use in proton exchange membrane fuel cells (PEMFCs). Significant cost reductions could be realized if PEMFCs were engineered to run on low-purity hydrogen, so efforts are underway to develop electrocatalysts with improved tolerance to CO poisoning. The CO tolerance of Pt electrocatalysts is well-known to be improved by alloying with Ru, but this is a relatively expensive raw material and further lowering of the potential of CO oxidation is sought. One alternative approach is to use tungsten oxide (WO_3) as a support or co-catalyst for Pt-based electrocatalysts, which has been shown to facilitate CO oxidation on Pt at potentials below that achieved by Ru. However, the detailed mechanism of improved tolerance is not fully understood, which is a bottleneck to fully exploiting this phenomenon.

In this work we use the combination of electrochemistry with *in situ* Raman spectroscopy and *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy to probe the mechanism of improved CO tolerance observed by physically mixing a commercial Pt/C electrocatalyst with WO_3. We conclude that the WO_3-assisted CO tolerance is imparted through a bifunctional mechanism, with the WO_3 itself mediating oxidation of Pt-adsorbed CO at potentials lower than in the absence of WO_3, as well as providing surface oxygen species. We also rule out an electronic mechanism (where the additive weakens the Pt-CO bond thus facilitating its oxidation) since our data in fact suggest a slight strengthening of the Pt-CO bond in the presence of WO_3. We discuss the implications of these insights on the potential application of WO_3 as a fuel cell catalyst additive, as well as providing a framework for distinguishing between the above mechanisms using complementary *in situ* spectroscopic techniques to characterize the roles of multiple components as a function of potential.

Towards Holistic Understanding of Electrochemical Energy Conversion and Storage Systems Using High Energy X-rays.

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Complete physico-chemical operando characterization of electrochemical devices in whole, or it's constituent materials separately, is necessary to guide the development and to improve the performance. High brilliance synchrotron X-ray sources play a crucial role in this respect as they act as a probe with relatively high penetration power and low damage potential. Synchrotron sources will undergo major upgrades in next decade and will provide even higher brilliance and, more importantly, coherence. These upgrades will be particularly advantageous for beamlines providing high energy X-rays as they will allow use of advanced scattering techniques with highly penetrating probe. Therefore, the techniques typically used for ex-situ measurements or at lower X-ray energies could be used on materials in liquid half-cells and operating electrochemical devices. In this contribution the new possibilities of using high energy, high intensity, coherent X-rays to probe model systems and whole electrochemical devices will be presented. The focus will be on defects tracking, local structure determination and correlative multimodal characterization using advanced WAXS, SAXS and surface scattering techniques.

To study fuel cells or batteries as a whole, elastic scattering techniques such as wide angle and small angle scattering are typically employed, as they can provide important complementary information to more standard X-ray imaging and tomography. The advantage is that the chemical contrast and sensitivity at atomic and nm scales is superior. Coupling these technique with the tomographic reconstruction (XRD-CT and SAXS-CT) is much less common as it requires bright synchrotron sources, fast 2D detectors and advanced instrumentation [1]. However, such combination allows spatial reconstruction of materials important atomic parameters in operando conditions. This will be demonstrated on imaging of standard 5 cm^2 PEM fuel cell during operation and Li-ion battery Si/C composite anode during charge and discharge.

Furthermore, local atomic and mesoscale structure, together with defect content, can also be determined by using Rietveld fitting, Pair Distribution Function (PDF) analysis and advanced SAXS theory. This in principle allows holistic investigations of interfaces at the device level, specification of defects' role in catalysis and determination of interplay between different phases during operation. These are critical questions needed to be answered in order to incorporate novel materials into the electrochemical devices. Examples will be given on studies of the defectous ORR catalysts [2,3] and amorphous Li-ion anodes.

HESXRD (High Energy Surface X-ray Diffraction) [4] and TDS (Transmission Surface Diffraction) [5] provide ideal tools to study structural changes during reaction conditions on single crystal model electrodes. The main advantage of both techniques is the possibility to follow the surface structural changes precisely with atomic resolution. While HESXRD is ideally used to determine exact atomic position, the TSD is easier from experimental perspective and allows studies with high spatial resolution. Advantages and disadvantages of both approaches will be discussed and examples of measurements on ORR and OER catalysts will be given. The future possibility to use high energy coherent beams will open new opportunities for both techniques to study single defects and surface dynamics in operando conditions.

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Germanium Oxide as Negative Electrode for Li-Ion Batteries – Phase Stabilization and Enhanced Electrochemical Performance *via* Fe Doping

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The transportation sector is continuously transitioning from combustion engines towards fully electric vehicles, and lithium-ion batteries (LIBs) are the energy storage device of choice due to their high volumetric and gravimetric energy density.[1] However, to meet future targets in terms of driving range and re-/charging times, the state-of-the-art graphite anode needs to be replaced with materials offering even higher energy densities and, especially, better power capabilities. Alloying metal-oxides such as ZnO and SnO_2 have been widely studied so far since they offer high theoretical specific capacities (966 mAh g^{-1} and 1494 mAh g^{-1}, respectively) at relatively low cost. Furthermore, such alloying metal oxides have high densities, which leads to substantially higher volumetric capacities compared to graphite. However, these high densities, in combination with the high overall Li^+ uptake, lead to pronounced volume expansion upon cycling. Furthermore, the eventually irreversible Li_2O formation limits the practically achievable specific capacity to the alloying contribution only. It has been shown that these detrimental effects can be overcome by introducing a transition metal (e.g., Fe, Co) into the lattice, leading to a reversible Li_2O formation and less pronounced volume expansion and, consequently, to capacities which are close to the theoretical values.[2,3] This concept of transition metal doping has also been transferred to germanium oxide – an example for an Li^+ alloying oxide with even higher theoretical specific capacity (i.e., 2152 mAh g^{-1}) – and was shown to partially enable re-oxidation of the germanium to germanium oxide, though (so far) only in the initial cycles.[4]

Within this study, we tackled the problem from a different perspective and elaborate on the effect of Fe in GeO_2 on the structural stability of different germanium oxide phases and, as a result, its electrochemical performance. The techniques employed include, amongst others, highly complementary *in situ/operando* characterization such as *in situ* high temperature XRD, *operando* XRD and *operando* dilatometry. The results on germanium oxide as a model compound shed light on a commonly overlooked impact factor for the electrochemical performance of such materials and, in fact, metal oxides in general.

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Staircase Voltammetry: The Effect of the Applied Potential Ramp on the HUPD in Cyclic Voltammograms of Platinum

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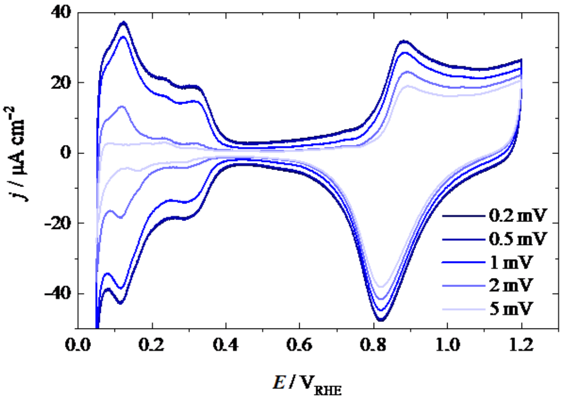
Although cyclic voltammetry (CV) is widely relied upon to interpret the behaviour of electrochemical systems, it is often overlooked that the measured responses depend not only on the studied system, but also on the applied settings and technical capabilities of the potentiostat. The main device-dependent variable is the type of the applied potential ramp, which can be either a truly linear or a stepwise function of time. While a linear change of potential is typically assumed for interpreting the results, most potentiostats operate with a digital ramp by default and a true analog ramp generator is only offered as an optional feature.

The analog ramp is defined by only one parameter – the scan rate – but a staircase function is also determined by the size of the potential step ΔE or the step duration Δt. Additionally, the delay time of a current measurement within the step duration ($\alpha \cdot \Delta t$) strongly affects the measured current response. Taking into account the technical differences among potentiostats and the user-defined variability, there are many ways of recording a cyclic voltammogram with a given scan rate. Despite this, detailed descriptions of the applied ramps and current recording modes are rarely reported as experimental conditions [1]. This practice is acceptable only when the results of a staircase ramp are equivalent to an analog experiment. But it is not obvious what set of conditions apply for a given electrochemical process. It is well established that surface reactions are more sensitive to the staircase shape than diffusive processes. [2] One such surface phenomenon is the hydrogen underpotential deposition (HUPD) on platinum electrodes, which is the most studied electrode material in electrocatalysis. Surprisingly, the practical effects of staircase ramp parameters on the HUPD response are not widely understood.

In this contribution, we showcase some experimental settings that can drastically affect the HUPD response on platinum when measured with a staircase potential ramp. The size of the potential step for a given scan rate was systematically varied, as was the parameter α of the current sampling delay. The settings that yielded a response equivalent to an analog ramp will be discussed. The advantages of averaging multiple current measurements within one potential step will also be demonstrated. This study aims to point out the pitfalls of the established practice of not reporting fundamental experimental parameters when studying the HUPD process on Pt electrodes.



Cyclic voltammograms of polycrystalline Pt electrode in 0.1 M $HClO_4$ recorded with different potential steps ΔE at a scan rate of 20 mV s^{-1}. The current was measured at the end of each potential step (α=1).

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Anodic Production of Hydrogen Peroxide on Carbon-based Materials

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The production of hydrogen peroxide (H_2O_2) using renewable electricity, oxygen (O_2) and water (H_2O) is an alternate ''green'' route to the current anthraquinone process[1]. There are two approaches for the electrochemical synthesis of H_2O_2. One pathway is the partial reduction of O_2 at cathodes employing either noble metal alloys or doped carbon. Another possible route is the two-electron oxidation of water to H_2O_2, which competes with the four-electron oxidation of H_2O to O_2[2]. This anodic production of H_2O_2 is desirable since it can be coupled with other cathodic reactions, such as CO_2 reduction reaction to valuable products. However, it remains a great challenge to develop efficient electrocatalysts for H_2O_2 anodic synthesis, which can suppress the thermodynamically favored oxygen evolution reaction (OER). The objective of our research is to identify the parameters that will allow maximizing the efficiency of the catalyst and the electrochemical process for the anodic production of H_2O_2. Carbon has been used as an electrocatalyst due to its large surface area, conductivity, chemical stability in alkaline electrolytes, and low cost. Selective oxidation of water to hydrogen peroxide on different carbon materials was conducted using a two compartment H-cell, where copper was used as a counter electrode. The impact of electrolyte concentration, current density, pH values of the electrolyte, temperature, and ion exchange membranes, have been investigated in order to optimize reaction conditions for the anodic production of H_2O_2. A concentration of 1.73 mM for H_2O_2 was achieved at the applied current density of 100 mA cm^{-2} in 2.7 M $KHCO_3$ electrolyte using a cation exchange membrane in a flow cell. (**Figure 1**).

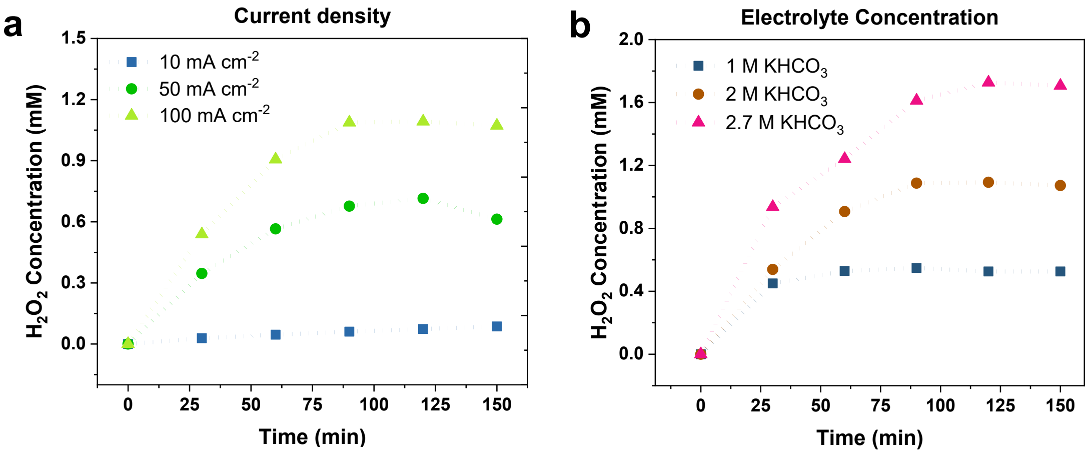

Figure 1: Hydrogen peroxide concentration in the anolyte during electrolysis at **(a)** different current densities using 2 M $KHCO_3$ and **(b)** in different electrolyte concentrations of $KHCO_3$ at 100 mA cm^{-2}

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Effect of secondary solution concentration on lithium electrodialysis using lithium ion electrolyte $Li_{0.29}La_{0.57}TiO_3$

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The demand for lithium resources is rapidly increasing with the production of lithium-ion batteries. Today's lithium is produced from brine or ore [1]. The issues of the former are long process time and large environmental burdens. The latter issue is the high cost for high purification [2]. To establish a better lithium recovery method, we have investigated lithium recovery by electrodialysis using lithium ion conductive solid electrolyte $Li_{0.29}La_{0.57}TiO_3$ (LLTO). The electrochemical impedance of electrodialysis is affected by the concentration of cations in solution. When this recovery is performed in a batch system, the lithium ion concentration of the solution changes as the recovery of lithium proceeds. Therefore, it is important to elucidate the influence of the lithium ion concentration in the solution on the electrochemical impedance. In this study, we investigate the effect of lithium ion concentration in the secondary solution on lithium recovery rate by electrodialysis using LLTO.

An anode (primary side) and a cathode (secondary side) electrodes were prepared on the surface of LLTO using a platinum paste. Reference electrodes was prepared on both surfaces of the LLTO at positions apart from the anode and cathode. A DC voltage of 2.0 V was applied between the anode and cathode. Electrochemical impedances were measured by the 3-terminal method using the reference electrodes and 2-terminal method. The primary side solution was a 1.0 M aqueous lithium hydroxide solution. The secondary side solution was pure water or an aqueous lithium hydroxide solution having a concentration of 10^{-3}-1.0 M. The amount of transferred lithium was estimated by Faraday's law using the current value.

As shown in Figure 1, the migration rate of lithium depended on the concentration of lithium ions in the secondary solution and reached a maximum at 10^{-2} M. The cause of this dependence was clarified by the AC impedance method.

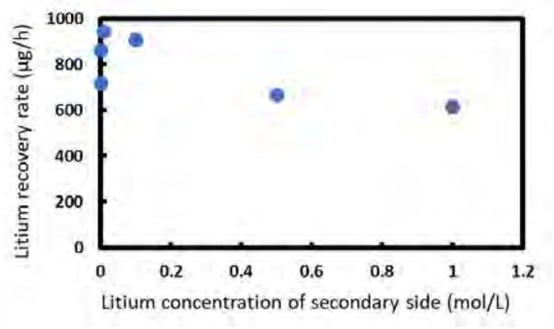

Figure 1 Lithium recovery rate at different lithium concentration in electrodialysis secondary solutions.

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Investigation of Aniline and p-aminodiphenylamine Oxidation Products formed using Fe_3O_4 NPs/H_2O_2 system: Structure and Electrochemical Behavior

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Polyaniline (PANI) is one of the most studied conducting polymers thanks to its simple synthesis and wide range of favorable properties [1]. In this work we present a comparative study of polymeric products obtained from two different monomeric species, aniline and p-aminodiphenylamine (p-ADPA) oxidized in similar conditions using Fe_3O_4 nanoparticles (NPs)/H_2O_2 catalyst/oxidant system. So far H_2O_2, as a clean oxidant (the product of its reduction is only water), has mostly been used in polymerizations catalyzed by enzymes. In our approach Fe_3O_4 NPs replace much expensive enzymes, while synthetic conditions are tuned to achieve good conductivity of products.

The process of p-ADPA oxidation occurred much faster than the oxidation of aniline, due to lower oxidation potential of p-ADPA, which is documented by the color changes of reaction mixtures and changes in UV-Vis spectra with time. Based on the structural characterization of products (PANI/Fe_3O_4 and Poly(p-ADPA)/Fe_3O_4) it was found that the oxidations of aniline and p-ADPA led to the formation of PANI in the electroconductive, half-oxidized form called emeraldine salt (ES) [1,2]. FTIR spectra of both products contain characteristic bands of PANI-ES and evidence that the materials have very similar molecular structure. On the other side, Raman spectra showed that there are some fine differences in the molecular structure of the two materials. The Raman spectrum of Poly(p-ADPA)/Fe_3O_4 contains some bands indicating the intramolecular oxidative cyclization in the polymer chains, which are absent in the spectrum of PANI/Fe_3O_4 sample. SEM images evidenced considerably different morphology of the two samples. PANI/Fe_3O_4 has heterogeneous morphology with a large content of regularly shaped microspheres, while Poly(p-ADPA)/Fe_3O_4 contains dominant plate-like morphology. Such differences in the materials' surface implicate that their electrochemical behavior differs largely, which was confirmed by cyclic voltammetry measurements (Fig.1.). The electrochemical behavior of both materials was tested in 1M HCl solution. The cyclic voltammogram (CV) of PANI/Fe_3O_4 shows typical redox pair of PANI: the dominating redox couple at lower potentials corresponds to the interconversion between nonconducting leucoemeraldine base and ES, and the redox couple at higher potentials corresponds to the interconversion between ES and fully oxidized pernigraniline salt form. In CV of Poly(p-ADPA)/Fe_3O_4 the redox pair at higher potentials is more pronounced and the two oxidation (reduction) peaks are merged. Differences in molecular structure and surface morphology of the two samples clearly support the electrochemical behavior and higher capacitance of PANI/Fe_3O_4 (~180 Fg^{-1}) in comparison to Poly(p-ADPA)/Fe_3O_4 (~50 Fg^{-1}), even though their electrical conductivities are of the same order of magnitude (10^{-2} Scm^{-1}). This makes PANI/Fe_3O_4 a better electrode material for charge storage applications.

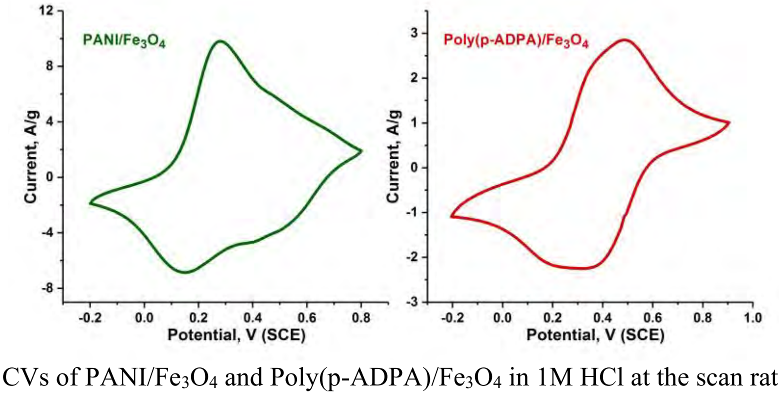

Figure 1. CVs of PANI/Fe_3O_4 and Poly(p-ADPA)/Fe_3O_4 in 1M HCl at the scan rate 20 mVs^{-1}.

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Three-dimensional $Na_4Fe_3(PO_4)_2P_2O_7/Na_2FeP_2O_7$ polyanionic heterostructure: the synthesis and electrochemical behavior in the aqueous lithium and sodium nitrate solutions

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Polyanionic compounds attract attention as a cathodic materials for Li- and Na-ion rechargeable batteries. The main advantages are open 3D framework capable of intercalating large amount of alkaline ions, an excellent thermal/structural stability and high safety. Mixed phosphate-pyrophosphate $Na_4Fe_3(PO_4)_2P_2O_7$ and pyrophosphate $Na_2FeP_2O_7$ possess attractive sodium insertion structures, displaying low activation barrier for Na-ion diffusion. The idea of this work is to hybridize these polyanionic phases through the control of synthesis conditions and capture each individual redox process during charging/discharging of the hybridized powder. By adjusting the synthesis conditions in the citric acid-assisted sol-gel process, followed by a heat treatment at 500 °C under Ar/5%H_2, the composite containing $Na_4Fe_3(PO_4)_2P_2O_7$ and $Na_2FeP_2O_7$ (denoted as NFPP/C) was synthesized, as confirmed by X-ray diffraction. The contribution of these phases was found to be ~29% for $Na_4Fe_3(PO_4)_2P_2O_7$ and ~71% for $Na_2FeP_2O_7$. Vibrational modes of PO_4^{3-} and $P_2O_7^{4-}$ groups are identified by means of Infrared and Raman spectroscopy. The total carbon content of 21.7 %, which originates from citric acid and sucrose, was determined by thermogravimetry in air atmosphere. Both cyclic voltammetry (CV) and chronopotenciometry (CP) indicate that NFPP/C behaves differently in Li- and Na-nitrate solutions, Fig.1. Comparative CV and CP curves, measured under common current conditions, reveal better intercalation ability of 3D polyanionic framework for Na- than for Li-ions. Individual redox processes of both $Na_4Fe_3(PO_4)_2P_2O_7$ and $Na_2FeP_2O_7$ phases can be recognized in CV of NFPP/C obtained at 1mV s^{-1} in $NaNO_3$. As a result, a very high specific capacity of ~ 108 mAh g^{-1} (at ~ 300mA g^{-1}) was measured in $NaNO_3$, while the corresponding value in $LiNO_3$ was ~ 69 mAh g^{-1}.

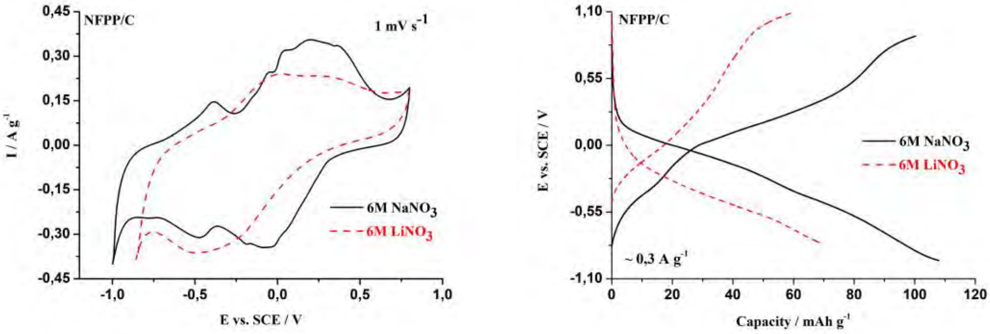

Figure 1. Comparative CVs (left, scan rate was 1 mV s^{-1}) and charge/discharge curves (right, current density was ~ 0,3 A g^{-1}) of the NFPP/C composite measured in $NaNO_3$ and $LiNO_3$ solution.

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Electrochemical Synthesis of $[Bi_6O_5(OH)_3](NO_3)_5\cdot 2H_2O$ by Electrodeposition from Water and Ethanol Bi^{3+} Solutions and Comparison of their Sorption Performance for Removal of Reactive Blue 19 from Water

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Abstract

Due to their large-scale production and extensive application synthetic dyes are the major industrial pollutants and water contaminants[1]. Because of that wastewater from dye production and application industries presents a serious threat to the environment. Adsorption due to its simplicity and high efficiency is one of the most often employed methods for the treatment of wastewater[2].

The aim of this research is electrochemical synthesis of basic bismuth nitrate from water and ethanol Bi^{3+} solutions and its application as a sorbent. The main advantages of electrochemical synthesis are simplicity, rigid control of film thickness, uniformity, deposition rate and low cost of equipment and starting materials[3]. Organic electrolytes have been usually used to realize a wide electrochemical window, avoid hydrogen embrittlement, improve the wettability of the electrode and improve anti-wear performance of deposit[4].

Materials were synthesized by galvanostatic electrodeposition in the two electrode cell with a Ti sheet as a substrate (cathode) and a stainless steel sheet as an auxiliary electrode (anode), followed by thermal treatment in air at 200 ºC. Electrodeposition was done from an acidic Bi^{3+} solution in water or 96% ethanol at constant current density of 150 mA cm^{-2} for 5 minutes. Obtained materials were characterized by SEM-EDX, XRD, BET and FTIR methods. The results of analyses showed that both materials (synthesized from water and ethanol solutions) are pure trigonal $[Bi_6O_5(OH)_3](NO_3)_5\cdot 2H_2O$ with high crystallinity. Morphologically, they are composed of aggregates which were formed of several smaller particles of various shapes and sizes, some smaller than 100 nm. According to the IUPAC classification the N_2 adsorption/desorption isotherms of materials are type II, which is related to unrestricted monolayer-multilayer adsorption and nonporous or macroporous adsorbents. The material synthesized from the ethanol solution has the specific surface area of 1.43 $m^2\ g^{-1}$, while the specific surface area of the material synthesized from the water solution is 0.95 $m^2\ g^{-1}$.

The sorption performances of these materials were investigated by removal of textile dye Reactive Blue 19 from water. The results showed that both materials have significantly higher sorption capacities comparing with the inorganic sorbents found in literature, making them promising means for the textile dyes removal from water[5–7]. The material synthesized from the ethanol solution has higher sorption capacity (1344.99 mg g^{-1}) than the material synthesized from the water (1049.19 mg g^{-1}). The main reason of improved sorption capacity by using ethanol solution is higher specific surface area of obtained material. Also, important characteristics of material synthesized from ethanol solution that affect a better sorption performance of that material is its higher hydrophilicity, i.e. higher tendency of getting solvated by water.

Acknowledgements

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Electrochemical Studies of Semi-transparent $NiCo_2O_4$/ITO Supercapacitor Electrodes

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A semi-transparent $NiCo_2O_4$/ITO electrode for supercapacitor applications has been prepared by an ink-printing method using a Dimatix 2D materials printer (Fujifilm) *(Figure 1)*. Structural and morphological characterization of the $NiCo_2O_4$ film was performed using XRD, SEM and AFM measurements. The average nanoparticle size in the film was estimated by SEM to be ca 100 nm whereas film thickness for films produced after two successive printing steps varied between 200-300 nm, as measured by AFM *(Figure 1)*. Film transparency in the 400-800 nm range was measured to be 35-50%. The electrochemical characterization of the $NiCo_2O_4$/ITO thin film electrodes was carried out by Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Galvanostatic Charge-Discharge (GCD) in 1 M NaOH electrolyte *(Figure 2)*. A nearly constant areal capacitance in the 30-25 mF cm^{-2} range is obtained for discharge rates up to 1 mA cm^{-2}. This is among the highest reported for very thin, transparent/semi-transparent supercapacitor electrodes [1-2]. The onset of capacitance loss at higher discharge current densities indicates electron transfer and/or reactant diffusion limitations of the associated faradaic reaction. In summary, the present work has proven the feasibility of preparing low cost and high performance binary metal oxide materials for semi-transparent supercapacitor applications, by a facile inkjet printing method.

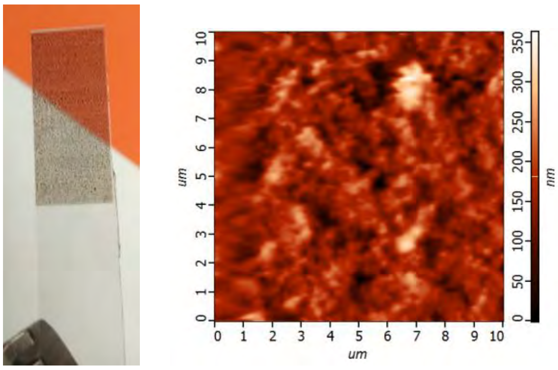

Figure 1 *Photograph (left) and AFM micrograph (right) of a semi-transparent printed $NiCo_2O_4$/ITO electrode*

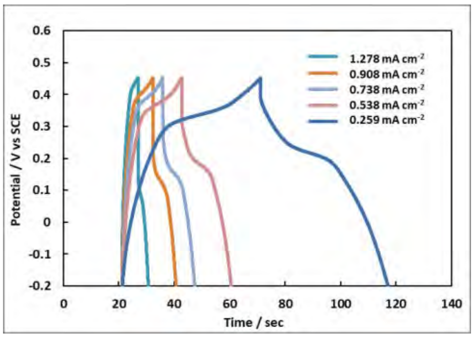

Figure 2 *Galvanostatic Charge-Discharge curves of a semi-transparent $NiCo_2O_4$/ITO electrode in 1M NaOH at various current densities*

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Understanding the Hydrogen Evolution Reaction Kinetics of Electrodeposited Nickel-Molybdenum in Acidic, Neutral, and Alkaline Conditions

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Effective water splitting via electrolysis driven by renewable energy requires highly active catalysts to minimize the sensitivity of the hydrogen generation rate to fluctuating operating conditions [1,2]. NiMo alloys can potentially replace platinum as hydrogen evolution reaction (HER) catalysts because of their low overpotential over the entire pH range [3,4]. However, the pH-dependent kinetics of NiMo are not fully understood. In addition, it is still not clear if the low HER overpotential of NiMo is caused by high intrinsic catalytic activity or by extrinsic factors, such as increased surface area or mass loading [5,6], which would have cost implications for large-scale hydrogen production. Herein we present a study of HER kinetics of NiMo electrodeposited on fluorine-doped tin oxide glass in alkaline, neutral and acidic media by polarization and electrochemical impedance spectroscopy (EIS) techniques.

The polarization measurements indicated that the high HER activity of NiMo film was caused by both its high active surface area and high intrinsic catalytic activity. In subsequent measurements, the NiMo films showed the lowest HER activities in neutral conditions and the highest activities in acidic conditions. We found that the higher HER activity in acidic media was accompanied by more favorable hydrogen adsorption and charge transfer kinetics than in neutral and alkaline media. While two different Tafel-slope regions were observed for acidic and neutral media, only one was obtained for alkaline conditions. The EIS results suggested that the change of Tafel-slope was caused by the increased hydrogen surface coverage at high overpotential region. In acidic and neutral media, both Volmer and Heyrovsky steps significantly affected the HER kinetics at the low overpotential region, while at high overpotentials the Volmer step limited the HER kinetics. In alkaline conditions, however, the HER rate was controlled by the Volmer step, and other steps were not visible in the EIS data.

NiMo films with different thicknesses were also measured in electrolytes with different pH and in all cases the thickest layers provided the best HER performance due to highest active surface area. Because the highest HER activity was due to surface area, initial performance optimization by increasing film thickness should be quite simple, but further development of deposition methods for even higher specific surface area could also prove beneficial.

This research was done under the PECSYS project. The project has received funding from the FUEL CELLS AND HYDROGEN 2 JOINT UNDERTAKING under grant agreement No. 735218. This Joint Undertaking receives support from the EUROPEAN UNION'S HORIZON 2020 RESEARCH AND INNOVATION programme and Hydrogen Europe and N.ERGHY. The project started on the 1st of January 2017 with a duration of 48 months.

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Sodium redox behavior of maricite $NaFePO_4$ in an aqueous electrolytic solution

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Since the discovery of the electrochemically active $LiFePO_4$[1], the three-dimensional frameworks built on transition metals and polyanions $(XO_4)^{n-}$ have experienced a huge expansion in the research field of alkaline-ion batteries. $NaFePO_4$ exists in two polymorphic structures: triphylite and maricite (thermodynamically more stable). The maricite $NaFePO_4$ phase was initially considered as electrochemically inactive for sodium rechargeable batteries, but somewhat later its activity was demonstrated[2]. In this paper, the maricite $NaFePO_4$/C composite, is synthesized in an unusual way, by targeting the stoichiometric composition of the $Na_4Fe_3(PO_4)_2P_2O_7$/C using the glycine-nitrate process and then applying the temperature corresponding to the structural decomposition of this polyanionic compound (650°C). XRD, FTIR and Raman spectroscopy observations of such obtained powder confirmed the formation of the maricite phase, while the cyclic voltammetry, measured in the electrochemical stability window of $NaNO_3$ aqueous solution, showed its electrochemical inactivity. By exposing the maricite phase to high anodic potentials in $NaNO_3$ (beyond the stable potential window), the redox peaks have appeared and electrochemical performance of the maricite itself is improved. Further holding the electrode at a deep positive potential (1.6 V vs. SCE) for a certain periodic time, results in the gradual increase of redox peaks, Fig.1a.The integrated surface area under CV curve of anodic or cathodic part (which corresponds to the specific capacity of the material) was increased by ~50%. The shape of redox peaks remains retained upon changing the scan rate, Fig.1b. To reveal what really happens at the $NaFePO_4$ surface under deep anodic polarization and what is the most responsible for the observed electrochemical activation, the activated powder was subjected to further characterization. Based on FTIR and Raman measurements, it can be concluded that the high anodic polarization results in the phase transformation of electrochemically inactive maricite $NaFePO_4$ to active $FePO_4$ phase. Whether the active phase is triphylite or amorphous maricite is still a question which will be addressed. The obtained results open novel directions regarding the use of $NaFePO_4$ in Na-ion rechargeable batteries.

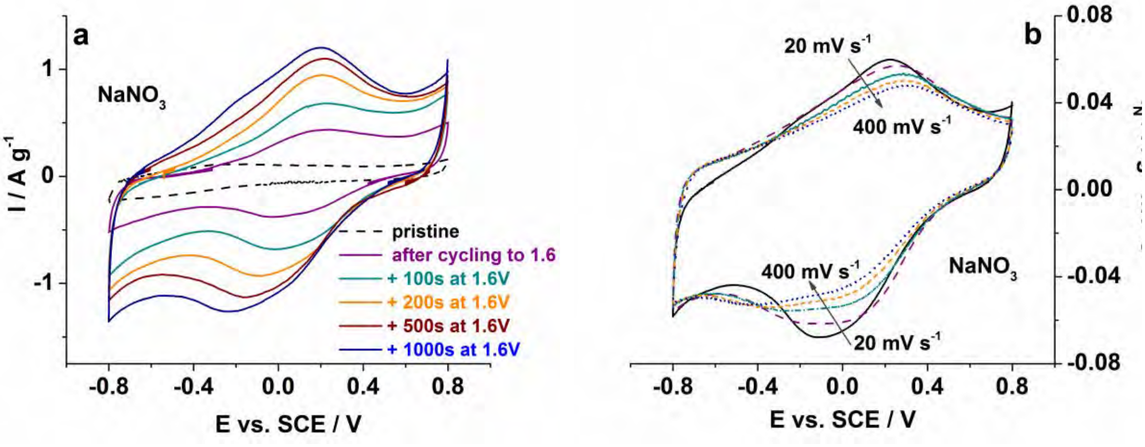

Figure 1.a) CVs of maricite NaFePO4/C before (pristine) and after anodic polarization, at 20 mVs^{-1}; CVs of activated $NaFePO_4$/C at different scan rates (b). The electrolyte is aqueous solution of $NaNO_3$.

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Scanning Electrochemical Cell Microscopy – Investigation of the Hydrogen Evolution Reaction on Thin Film Dichalcogenides

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The usage of fossil fuels as energy source and the excessive emission of CO_2 into the atmosphere is proven to be a major threat for the environment. Therefore, the research on sustainable and efficient energy storage and alternative fuels is of great importance. Hydrogen can be produced using renewable energy via water electrolysis but catalyst materials are required to run the reaction efficiently. For the electrocatalytic evolution of molecular hydrogen, materials based on noble metals such as Pt and Pd show the highest activity. Due to the cost-intensity of rare precious noble metals the development of active and stable non-noble metal based electrocatalysts for the hydrogen evolution reaction (HER) is promoted.[1]

In recent years, thin film dichalcogenides, like MoS_2 and WS_2, have been established as promising candidates for the HER and various reports indicate that the edges and defects show higher catalytic activity compared with the basal plane.[2] Aiming on materials with increased activity defect engineering comes into focus. One approach for a controlled formation of defects into thin film materials is the irradiation with ions that also results in an increase of the catalytic activity for the HER.[3]

Different electrochemical methods can be used to evaluate the electrocatalytic activity of materials. From this, scanning electrochemical cell microscopy (SECCM) was established in the recent years as a powerful tool to assess the electrocatalytic activity of different materials at nanoscale. Using pulled nanocapillaries as probes, measurements can be performed utilizing electrolyte droplets in the size of less than 100 nm as electrochemical cells. This results in an unparalleled resolution in the observation of electrochemical reactions leading to a better understanding of catalytically active sites or intrinsic activity of a single catalyst particle.[4,5]

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IrO_2/Ir/Ti and IrO_2/Ir(Ni)/Ti Oxygen Evolution Anodes prepared by Galvanic Deposition and Galvanic Replacement

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IrO_2-modified Ti electrodes have been prepared by either a simple galvanic deposition process or a Ni-mediated galvanic replacement method. In the former case a freshly etched Ti substrate has been treated with an Ir(IV) solution, resulting in the spontaneous deposition of metallic Ir on the surface of the Ti substrate with the simultaneous oxidation of nearby freshly etched Ti sites [1]. In the latter case, a smooth Ni film has been electrodeposited on the Ti substrate from a Watts bath and its surface layers spontaneously exchanged with metallic Ir upon treatment with an Ir(IV) solution [2-3]. Anodization of the resulting Ir/Ti and Ir(Ni)/Ti electrodes by means of continuous potential cycling in acid solutions resulted in the formation of IrO_2 porous surface layers (or IrO_x, depending on the positive potential limit), showing typical Ir oxide surface electrochemistry (*Figure 1*). SEM pictures revealed that the thus prepared IrO_2/Ir/Ti electrode is made of sparse IrO_2/Ir micrometer-sized islands and nanoparticles, while the IrO_2/Ir(Ni)/Ti electrode consisted of a continuous film with a nodular morphology (as confirmed by AFM). The composition of the coatings was estimated by EDS and XPS spectroscopy while Ir mass loading was determined by ICP-MS following etching in acid. These electrodes have been tested as oxygen evolution reaction (OER) anodes by slow potential sweep voltammetry *(Figure 2)*. IrO_2/Ir/Ti electrodes exhibited mass specific activities for OER (ca 200 mA mg_{Ir}^{-1} at η=300 mV) better or comparable to traditional Ir DSAs [4] or state-of-the-art thin thermal films [5], whereas the IrO_2/Ir(Ni)/Ti electrodes were proven comparable or better than both state-of-the art thin thermal films [6] and nanoparticle $IrNiO_x$ catalysts [7] (ca 2 A mg_{Ir}^{-1} at η=300 mV). The recently established enhancement of IrO_2 OER activity by Ni, combined with the widespread use of Ti as a stable electrode substrate, make IrO_2/Ir(Ni)/Ti attractive DSA electrodes.

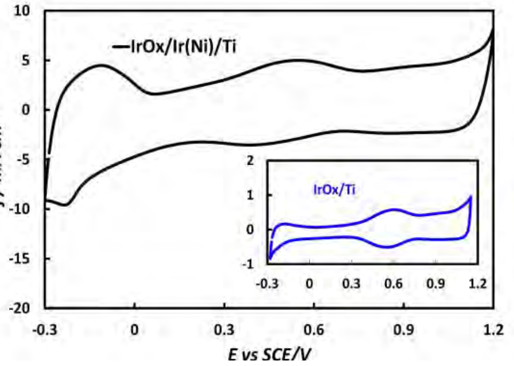

Figure 1 *Cyclic voltamograms (at 100mVs^{-1}) of IrOx/Ir(Ni)/Ti and IrOx/Ti (Inset) electrodes in a 0.1 M deaerated $HClO_4$ solution*

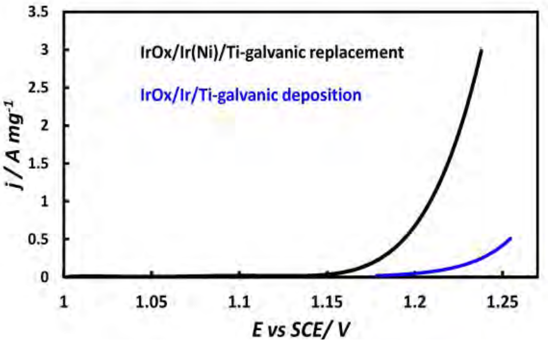

Figure 2 *Linear sweep voltamograms (at 5mVs^{-1}) of IrOx/Ir(Ni)/Ti and IrOx/Ti (Inset) electrodes in a 0.1 M deaerated $HClO_4$ solution*

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Surface-alloying During Pb Underpotential Deposition on Au and Cu

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Surface-alloys can form spontaneously during the deposition of one metal onto another, especially in systems with a very large lattice mismatch that do not have bulk counterparts (so-called immiscible systems). The spontaneous surface alloying has been widely studied in Ultra High Vacuum (UHV) [1], but these new materials have not been exploited much in practical applications. Because the high control and scalability make the transfer to real and practical systems viable and versatile, surface-alloying in an electrochemical environment is an ideal route to the design of new functional materials.

In this study, we have investigated the surface-alloying process during underpotential deposition (UPD) of Pb on Au(111) [2,3] and Cu(100) in the presence of various anions, e.g. perchlorate, chloride or bromide. This phenomenon has been studied using several electrochemical protocols such as repeated potential cycling over a limited UPD range (as illustrated in Fig. 1) or polarisation at a fixed potential in the UPD region. By following the changes in electrochemical behaviour, we established the range of potentials and conditions at which the surface-alloys form and quantified their composition. In addition to that, we investigated the structural and compositional changes by surface sensitive techniques such as in-situ Scanning Tunneling Microscopy (STM), X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), Energy-Filtered Photoemission Electron Microscopy (EF-PEEM) and Work Function (WF) mapping.

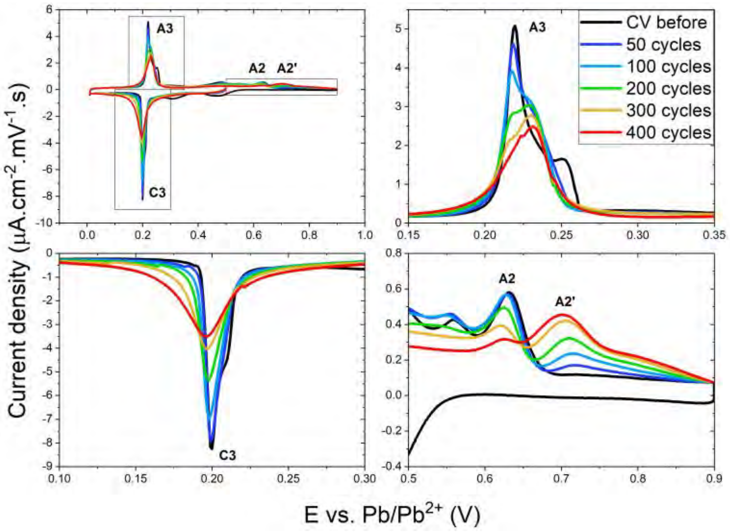

Fig. 1. Cyclic Voltammetries of Pb UPD on Au(111) in 1 mM Pb(ClO_4)$_2$ + 0.1 M $HClO_4$ solution after different numbers of potential cycles. Scan rate 10 mV/s.

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Investigating The Effect of Thiourea on The Electrorefining of Copper with An Extended Operando ORP-EIS Technique

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Electrorefining is an essential technique to obtain pure (LME grade A) copper. During this process a consumable and impure copper anode is placed near a steel cathode. A direct current supplies the necessary energy to oxidize the anode (dissolve the copper in the electrolyte) and reduce (deposit) the dissolved copper onto the cathode while impurities remain in the refining bath, resulting in a pure copper cathode [1]. Electroplating processes need the support of additives, which are added to produce smooth copper deposits without nodules and striations [1]. In the case of electrorefining is thiourea one of the common additives. The thiourea concentration decreases, during the time span of the electrorefining, since it partially becomes incorporated in the cathodes and partially reacts with cupric ions to form formamidine disulfide (FDS) [1]. This evolution in additive composition subsequently affects the copper deposition. An EIS study of copper plating with and without certain additives is already performed by Gabrielli [2] and Gladysz [3] to name a few. Although, to the best of our knowledge, the effect of thiourea and FDS on the copper plating is not yet investigated to the fullest.

We perform operando Odd Random Phase EIS (ORP-EIS) measurements on the copper reduction system by applying the sum of a bias current and a multisine signal. This allows us to study the effect of thiourea on the copper reduction process. With ORP-EIS we are able to quantify the impedance, noise, non-linearities and non-stationarities at the measured frequencies [4] and to quantify the non-stationarities of a linear system by estimating a time-varying impedance [5]. An extension of this technique allows us to model weak non-linear and non-stationary systems and to calculate the uncertainty intervals -containing: noise, non-linearities or both- at every time interval and around every measured frequency of the instantaneous impedance. The estimation of the instantaneous impedance and the quantification of the non-linearities in the non-stationary system enables us to approach the transfer function of the systems as close as possible.

In our study we notice the presence of non-linearities, even and odd, even with an RMS potential value of 10mV or less for the multisine output signal. We also discovered non-stationarities, present by skirts at the even and odd non-excited frequencies, and calculated the time evolution of the impedance spectra. Both observations, non-linearities and non-stationarities, demonstrate the importance of our technique in this research.

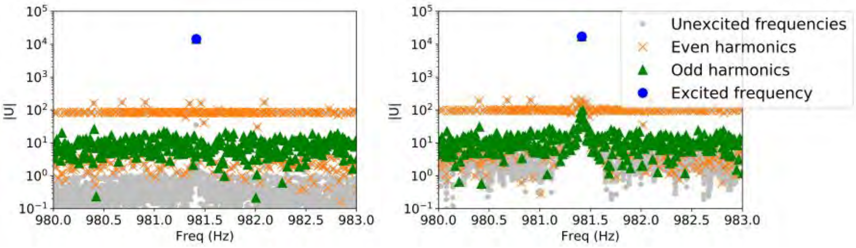

Figure: The presence of non-linearities (left) and skirts (right) in the frequency domain of the output potential signal.

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Functionalization of Polycrystalline Au Electrodes with Glycosylated Poly(acryoyl hydrazide) for the Electrochemical Detection of Cholera Toxin

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According to the World Health Organization up to 1 in 10 people fall ill and around 400,000 die every year all over the world after consuming contaminated food and/or water[1]. Foodborne diseases do not only affect the wellbeing of individuals but hinder the socio-economic development of communities through the loss of days of school and work, medical costs and economic losses. One of the main vectors of food/water contamination are bacteria.

The standard methods of detection of bacteria, based on cell culture, are reliable but present a very important drawback: detection times extend into days making it difficult to stop outbreaks. Other faster methods are too complex or expensive to be used in most affected populations.

Electrochemical biosensors are a promising alternative with their high sensitivity, simplicity, low-cost, fastness and portability[2]. Herein we present the first stages of development of an electrochemical biosensor for the detection of the subunit B of the cholera toxin (CTB). Galactose (Gal) was used as a biorecognition element to mimick the mechanism of recognition of our intestinal cells by CTB.

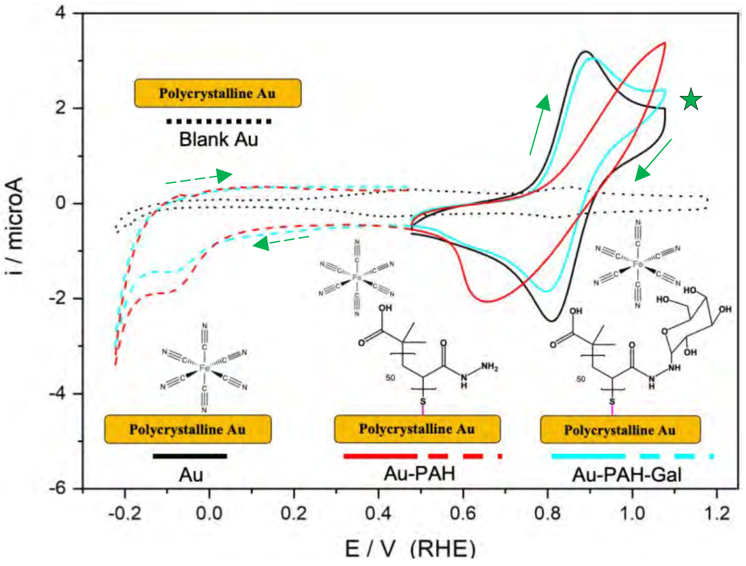

Fig. 1 – *CV characterization of polycrystalline Au electrode with redox probe [K$_4$Fe(CN)$_6$]; dashed lines indicate stripping processes.*

A polymeric linker, poly(acryloyl hydrazide) (PAH)[3], was employed to immobilize Gal on the surface of a polycrystalline Au electrode (Au-PAH-Gal): first, Gal was coupled to PAH (PAH-Gal); then, PAH-Gal was adsorbed onto the electrode from aqueous solution.

Cyclic voltammetry (CV) and a redox probe [K$_4$Fe(CN)$_6$] were used **(Fig. 1)** to study the surface of the electrode modified with PAH (Au-PAH, red scan) and PAH-Gal (Au-PAH-Gal, blue scan). For Au-PAH the voltammogram indicates, either a diffusion limited process across the layer; or a much slower electron transfer. With Au-PAH-Gal, only an attenuation of the signal of the probe with respect to the obtained on the bare electrode (black scan) is observed. The stripping peaks at low potential (dashed scans) corroborated the adsorption of PAH and PAH-Gal on the electrode.

These results point towards the immobilization of Gal on the electrode surface. The signal obtained with Au-PAH was probably due to a slower electron transfer forced by the chelating character of the hydrazide groups[4] of PAH. Another redox probe, FcMeOH, will be used to study this circumstance.

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Evidence of Lead Ions Detection on Azulene Based CMEs by Voltammetry

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Chemically modified electrodes (CMEs) based on 2-(azulen-1-yldiazenyl)-5-phenyl-1,3,4-thiadiazole (**L**) has been prepared for heavy metal ions recognition [1, 2]. **L** electrochemical characterization was carried out by CV, DPV and RDE. The film formation has been evidenced by cyclic voltammetry, electrochemical impedance spectroscopy, atomic force microscopy and scanning electron microscopy [3].

Different conditions for CMEs preparation have been examined. **L** direct electropolymerization by controlled potential electrolysis lead to the immobilization of **L** complexing monomer on the electrode surface. The complexing properties of **L** and poly**L** have been investigated towards heavy metal ions in water solutions by anodic stripping technique. The obtained results confirmed that CMEs are sensitive tools for lead ions identification and detection in comparison to Cd(II), Cu(II), Hg(II) ions.

Acknowledgement

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Mixed Oxide Electrodes Based on Ruthenium and Manganese. Influence of Precursor Salts on the Electrochemical Performances.

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Thin-film of metals oxides coating titanium supports (MMO films) have been extensively used in industry for a long time. Several metals and various compositions have been used for the construction of electrodes, in particular for the treatment of wastewater.

In previous works [1], [2] we have prepared different types of MMO and studied their electrochemical performances. In a standard procedure, the films were obtained by drop-cast. This method is very simple but unfortunately, it is not easy to obtain a uniform and well-controlled film.

In this work, electrodes coated with thin-film of ruthenium (RuOx) and manganese oxide (MnOx) were fabricated by thermal decomposition after deposition on a titanium substrate by spin-coating, a more accurate and controllable technique. In particular, we studied the influence of different salt precursors on the electrocatalytic properties. The investigated salts were: Ruthenium (III) acetylacetonate (Ru(acac)3), Ruthenium(III) chloride (RuCl3·xH2O), Manganese(II) nitrate (Mn(NO3)2·4H2O) and Manganese(III) acetylacetonate (Mn(acac)3).

A ruthenium salt and a manganese salt were mixed in a 1:1 molar ratio and dissolved in an organic solvent. Organic solutions were spin-coated on titanium foil (Ti) with a multilayer approach. All titanium substrates were previously cleaned by ultrasound treatment and then used as is or with a further HF etch.

The aim of this work was to determine if and how the specific combination of salt precursors could influence the morphology and the electrochemical performances.

A scheme of prepared substrates is reported in table 1.

Table 1

Id	Ti surface	Ru salt	Mn salt
1	smooth	$RuCl_3$	$Mn(acac)_3$
2	etch	$RuCl_3$	$Mn(acac)_3$
3	smooth	$Ru(acac)_3$	$Mn(acac)_3$
4	etch	$Ru(acac)_3$	$Mn(acac)_3$
5	smooth	$Ru(acac)_3$	$Mn(NO_3)_2$
6	etch	$Ru(acac)_3$	$Mn(NO_3)_2$

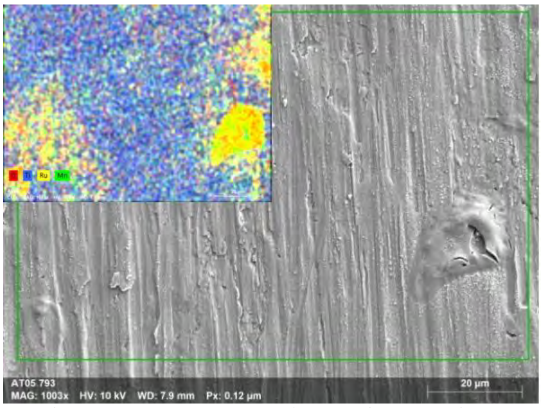

Figure 1: SEM & EDX image for sample 5

The thin-film electrodes were characterized by scanning electronic microscopy (SEM) and X-ray diffraction (XRD). In figure 1 is presented the SEM image for sample 5.

The electrochemical activity was investigated by potentiodynamic polarization, cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

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Sn-Cu-Ni Ternary Alloy Solders Electrodeposited from Deep Eutectic Solvents

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As a result of the imposed restrictions on the use of hazardous materials by electronic industries, an increased interest was focused towards the development of cost-effective lead-free solders. Candidate additives that are usually introduced to improve the performance of solder alloys include Ag, Cu, Ni, Bi, In, Zn, rare elements and nanoparticles. Sn-Cu based solders with nickel additions are considered as lower-cost alternatives to the well-known Sn-Ag-Cu ones [1].

Electrodeposition represents a faster and cheaper route suitable to synthesize solder layers, with a great potential for scaling up to industrial level production. Moreover, in the last decades the use of electrolytes based on deep eutectic solvents (DESs) was considered as a "greener" route for a large range of metals and alloys. Compared to classical aqueous electrolytes, the DESs allow the obtaining of quite constant alloys composition without the addition of surfactants, grain refiners, brighteners or oxidation inhibitors, thus providing an easier bath control especially for binary and ternary alloys electrodeposition.

Here we report the synthesis and characterization of the Sn-Cu-Ni alloy electrodeposited from choline chloride-ethylene glycol (denoted ILEG) eutectic mixture containing 500mM $SnCl_2$+0.055 mM $NiCl_2$+0.345 mM $CuCl_2$. The alloys were electrodeposited onto Cu substrate under direct and pulse current conditions. The influence of several operation parameters such as: the electrolyte temperature, the applied current density and pulse frequency on the morphology and crystallite size of the final alloy deposit has been investigated and discussed. The objective was to optimize the main operation parameters in order to achieve the corresponding alloy composition (Sn99.4Cu0.6 + Ni) able to possess the eutectic or near eutectic melting temperature of about 227 °C.

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Electroanalytical characterization of polysulfides (S_X^{2-}) in model solution and euxinic seawater conditions

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Sulfur (S), an ubiquitous element in the environment, occurs in different oxidation states from -2 (sulfide, S^{2-}) to +6 (sulfate, SO_4^{2-}). Between the thermodynamically stable end members (S^{2-}, SO_4^{2-}), a variety of intermediate S species exist, examples of which are sulfite, polythionates, thiosulfate, elemental sulfur (S^0), and polysulfides (S_X^{2-}). S species with intermediate oxidation states are produced during a variety of biotic and abiotic processes including the oxidation of hydrogen sulfide (HS^-) and sulfide minerals, SO_4^{2-} reduction, and the transformation of organic S compounds. Reduced forms of S, reduced sulfur species (RSS: S^{2-}, HS^-, S^0, S_X^{2-}, RSH), are most important forms for processes related to S biogeochemistry and environmental quality [1, 5]. Polysulfides are important RSS which play a role in numerous environmental processes, and so far there is not methodology for their direct determination in natural water environments, and conditions with presence of other RSS.

In this work for the first time differential pulse voltammetry (DPV) at the Hg electrode [1], was used for determination of S_X^{2-} in natural euxinic seawater environment (Rogoznica Lake, pH=7.0 - 7.5; oxygen concentration = 0 – 0.4 mg L^{-1}), i.e. conditions where total RSS (mainly in form of HS^-) could varied between 10^{-8} M to 10^{-3} M [2, 5]. In this approach an adsorption phenomenon associated with S_X^{2-} or a product of it's cathodic reaction with the Hg electrode created a characteristic current minimum at -1.0 V (vs.Ag/AgCL), which magnitude is proportional to the concentration of S(0) existing in the form of polysulfidic sulfur [1]. In our case, well defined DPV peaks were recorded for model K_2S_X (42% K_2S basis) NaCl/$NaHCO_3$ carbonate buffer solution (pH~9.5) in the concentration range between 10 mg L^{-1} and 500 mg L^{-1} (Figure 1a). The same approach, and obtained calibration, demonstrated presence of S_X^{2-} in the chemocline and anoxic euxinic layer of Rogoznica Lake, in the concentration range between 18 mg L^{-1} to 75 mg L^{-1} (Figure 1b). Additionally, sampled DC polarography (SDC) at the Hg electrode revealed in the studied samples a ratio between anodic and cathodic currents, i.e. the ratio between sulfide and S(0) presence in the S_X^{2-} [1,2]. Established electrochemical approach for RSS determination [2-5], based on accidification and purging step, determined total concentration of RSS and presence of its volatile and non-volatile fractions.

Concentration of S_X^{2-} as well as total RSS varied with environmental conditions (depth, oxygen concentration, light intensity) that are seasonaly dependent (Figure 1b).

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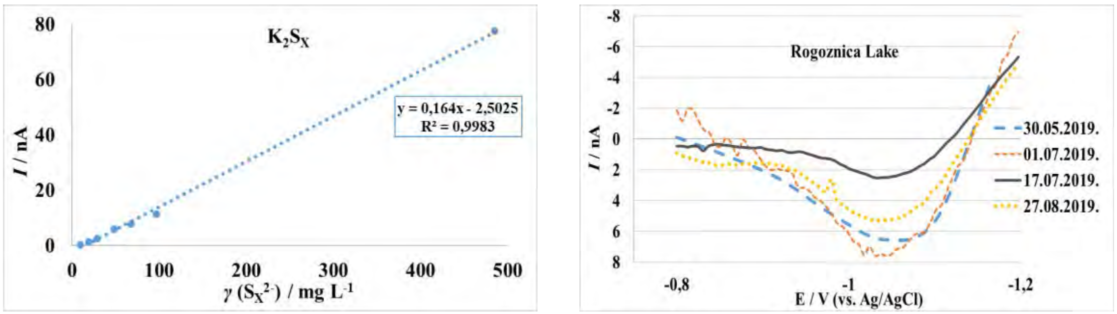

a) b)

Figure 1. a) Calibration curve for model polisulfide K_2S_X; b) DPV voltammograms of natural euxinic seawater samples recorded between 8 – 11m depths

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Ion transfer voltammetry of drugs at the liquid-liquid interface towards electrochemically controlled crystallization

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The development of new crystallization methods for sparingly soluble drugs is a subject of constant interest since 50% of the products are organic salts, which polymorphs may have different activity, bioavailability, toxicity or solubility[1]. A novel class of pharmaceutical substances which can improve these properties are co–crystals of drugs. Such homogeneous crystalline materials may contain two or more components incorporated in crystal lattice in definite stoichiometric amounts. Pharmaceutical co-crystals can incorporate pharmaceutically acceptable guest molecules into a crystal lattice along with the API (active pharmaceutical ingredient) and simultaneously not affecting pharmacological activity the drug[2].

In this work, the formation of crystals (co-crystals) by using ion-transfer processes at the interface between two immiscible electrolyte solutions (ITIES)[3], the control of the crystallization process by means of electrochemistry. For the purpose of this study, three drugs with low solubility in water, chemical structure proper for creation of co-crystals, amphiphilic properties with $0 < \log P < 3$, and bearing an electrical charge were selected: piroxicam[4], sildenafil[5] or diclofenac[6]. Such drugs are classified as a Class II API (low solubility and high permeability) based on the Biopharmaceutics Classification System.

Cyclic voltammetry at ITIES and μITIES was used to investigate of the ion transfer from an organic phase to an aqueous phase and to initiate precipitation of crystals (co-crystals). The selected drugs were dissolved in the organic phase in ionic form to allow the transfer of cationic or anionic form of the drug into the aqueous phase with the aim of forming insoluble drug (co-)crystal on the aqueous side of the liquid-liquid interface. A range of experimental parameters: nature of the drugs, composition of both organic and aqueous phases, nature of the polarization (electrochemical or chemical), dimension of the interface (macro- or microscopic) were investigated to control the interfacial processes and induce the formation of drug crystals. Such an electrocrystallization process at the ITIES will open new opportunities for the formation of organic drugs crystals.

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Electrochemical-Mechanical Characterisation of Energy Storage Materials

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The in-situ/operando mechanical behavior of materials for electrochemical energy storage is an important factor, having a major influence on the cell performance and ageing phenomena. There is a broad variety of materials and involved reaction mechanisms, displaying a specific impact on the mechanical properties during battery operation. For example, the process of Li ion intercalation into the active material is typically accompanied by accumulation of mechanical stress, which is followed by volume increase, deformation, disintegration or phase transition [1,2]. Most of the alloying and conversion materials experience a huge volume expansion when accommodating Li [3]. Furthermore, considerable change of the mechanical properties of structures for next generation batteries (e.g. sodium-, potassium intercalating and polymer active materials) has been detected as well [4,5].

Depending on the material structure and reaction mechanism the cumulative impact of these phenomena can finally result in a deteriorated performance, i.e. considerable reaction irreversibility and capacity loss. Therefore, the in-situ characterization of these processes and minimizing the induced mechanical stress and the subsequent material disintegration are amongst the major challenges on the road to the effective and safe battery operation.

The current talk will provide a brief overview and corresponding discussion on the recent achievements in our lab, related to the in-situ characterization of the mechanical properties of electroactive materials for reversible energy storage. The presentation will comprise several sub-topics, including, 1) reversible and irreversible volume change of battery materials (Li intercalating materials, electroactive polymers and electrodeposited silicon layers); 2) Impact of the external pressure on the electrochemical performance; and 3) actual strategies for modeling of the electrochemical-mechanical behavior.

The main techniques employed in our studies are electrochemical dilatometry (ECD) [6,7], electrochemical measurements under external mechanical load [8], electrochemical quartz crystal microbalance with damping monitoring (EQCM-D) [9] and finite element method (FEM) [8].

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Electrochemical Sensor with Redox Cycling in Nano-space for Highly Sensitive Detection of Endotoxin

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Many approaches are proposed to improve the sensitivity of electrochemical sensors. Among them, the redox cycling in nano-space which amplifies amperometric current by repeating reduction and oxidation of redox molecules at neighboring electrodes in nano-scale applied at different potentials is an especially powerful tool for a highly sensitive electrochemical sensor[1, 2]. In this research, we applied redox cycling to the endotoxin sensing[3] which requires high sensitivity for medical safety. Previously, we successfully developed an electrochemical endotoxin detection method with detecting *p*-aminophenol (pAP) liberated from peptide-conjugated pAP (LGR-pAP) by *Limulus* amebocyte lysate (LAL) reaction[4]. Here, we detected pAP using redox cycling in nano-space for ultra-high sensitive endotoxin sensing (Fig. 1).

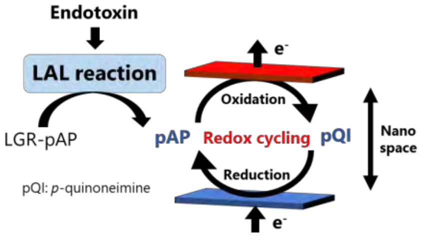

Fig. 1 The principle of this study

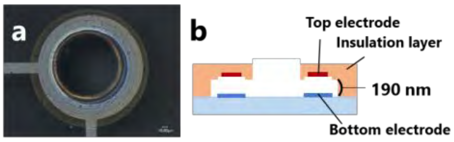

Fig. 2 Nanogap device. (a) Optical image. (b) Illustration of cross-sectional view.

First, the device with a pair of electrodes facing each other across a 190 nm gap was fabricated using photolithography and sputtering. Ti/Pt bottom electrode, Cr sacrificial layer, and Pt top electrode was deposited onto glass slide with lift-off process. An insulation layer was fabricated on the device except for sensor area using SU-8 negative photoresist. Finally, the sacrificial layer was removed by etching, and then the nanogap device was obtained (Fig. 2a and b). Characterization of the nanogap device was performed using cyclic voltammetry (CV) with 500 µM ferrocenemethanol (FMA) dissolved in 0.1 M KCl introduced onto the device. An Ag/AgCl electrode was used as a reference and a counter electrode. The potential of the bottom electrode was biased at 0.0 V, while the bottom electrode was swept at a scan rate of 20 mV/s. CV of non-redox cycling condition was also simulated using COMSOL Multiphysics with the model of the nanogap device without the bottom electrode. Finally, endotoxin assay was performed using 0.5 mM LGR-pAP as substrate for LAL reaction. After 60 min of LAL reaction, the solution was introduced onto the nanogap device, and then the current of the bottom electrode biased at -0.2 V was monitored while the top electrode was stepped from -0.2 V to 0.5 V.

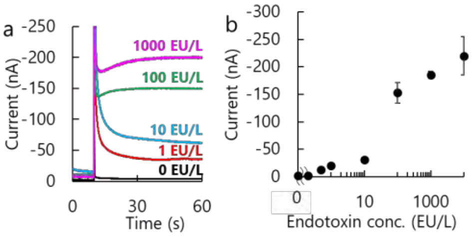

Fig. 3 Endotoxin assay. (a) Amperograms. (b) Calibration plots (n=3).

From the result of CV for FMA with redox-cycling condition, the cycling efficiency (the steady-state current from the bottom electrode/the steady-state current from the top electrode) of the nanogap device was 98%. This result indicates almost all of oxidant generated at top electrode reached the bottom electrode. Comparing to the CV with redox-cycling condition and non-redox cycling condition, the current was amplified by 1680 fold by redox cycling. These results showed that our nanogap device can be used for highly sensitive sensor. From the result of the endotoxin assay, the detection limit was 0.2 EU/L with 60 min of LAL reaction time. This result showed the sensitivity was improved by 5 fold comparing to our previous study[2]. This nanogap device can be used for sensitive, rapid and easy-to-use endotoxin sensing system to ensure the medical safety.

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Modeling of Droplet Formation During Lithium Dissolution

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Lithium metal anode batteries are promising candidates for next-generation energy storage systems as they have a high theoretical energy density. The cyclability has to be improved to make them commercially viable. It is limited by the irreversible loss of active lithium due to the formation of a solid electrolyte interface (SEI) and the formation of unreactive “dead” metallic lithium. The latter is the dominating source of capacity loss in certain battery systems [1]. Experiments show that during the dissolution of lithium whiskers, the tip cannot be dissolved, hint that mechanical instabilities occur [2]. We developed a generalized phase-field model of the dissolution process to gain insights into the underlying mechanisms of “dead” lithium formation and capacity fade.

Our phase-field model describes the dissolution of a single lithium whisker in a liquid electrolyte based on lithium surface tension and the interaction between lithium and the SEI, utilizing the framework of non-equilibrium thermodynamics [3,4]. We study the shape evolution of the lithium whisker under galvanostatic conditions and under which circumstances instabilities occur. Our model predicts the nucleation of a Rayleigh instability induced by interactions with the SEI. Thus, the lithium whisker does not dissolve completely, and an electrically disconnected metallic lithium droplet is formed (Fig. 1). This is in agreement with optical microscope observations of lithium dendrite dissolution [2].

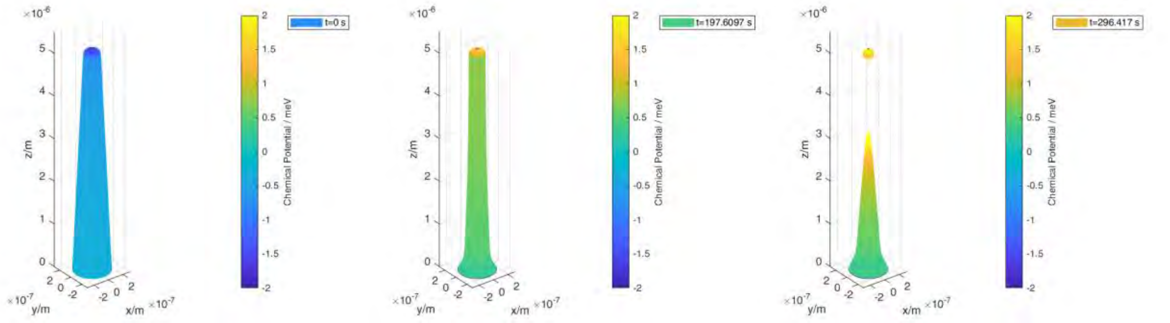

Figure 1: Droplet formation during galvanostatic discharge at different times. The dendrite tip disconnects from the base and a stable droplet forms while the rest of the dendrite dissolves.

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Investigation of Solvothermally Prepared $NaTi_2(PO_4)_3$ Nanocubes as Anode Material with High-Rate Capability for Aqueous Na-ion Batteries

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Recently, NASICON-structured $NaTi_2(PO_4)_3$ (NTP) has attracted a lot of attention as potential Na-ion battery material. This 3D open framework structure exhibits great potential for long cycle life due to strong covalent P-O bond and insignificant volume changes during sodium ion insertion/extraction. Moreover, it shows high Coulombic efficiency, good thermal stability, excellent rate capability for reversible intercalation of two sodium ions per formula corresponding to a theoretical capacity of 133 mAh/g at ~2.1V vs. Na^+/Na. In addition, its favorable potential, low cost and environmental friendliness makes NTP a good candidate as anode material for aqueous sodium ion batteries [1]. However, its poor electronic conductivity affects the sodiation kinetics and overall performance as an electrode material. Two common methods have been reported for improving the NTP electrochemical properties: reducing ionic and electronic transporting path by decreasing the particle size and by particle surface coating with carbon or other conductive additives [2].

In this study, NTP nanoparticles were synthesized via solvothermal method using ethanol by heating the mixture at 180 °C for 12 hours. Powders were coated with glucose and calcinated at 700 °C for 2h in nitrogen atmosphere. The average size of nanocubes was 70 ± 9 nm (Fig. 1a). The slurry for the working electrode was prepared by mixing 70 wt% of active material, 20 wt% of carbon (Super-P, TIMCAL) and 10 wt% of polyvinylidene fluoride (HSV1800, Kynar) in N-methyl-2-pyrrolidone (Sigma Aldrich, 99.5 %) solvent. After ball-milling the mixture for 1 hour at 900 rpm, it was coated on stainless steel mesh and dried in vacuum (120 °C) for 3 hours. The electrochemical performance of the synthesized samples was measured in a three-electrode beaker-type cell with Ag/AgCl as reference and graphite rod as counter electrodes in 1M Na_2SO_4(aq.) electrolyte.

The results show the material capable of extremely high-rate cycling performance even up to the rates of 100C (~13.3 A/g) with relatively slow degradation on cycle number. However the low-rate performance at 0.1C – 1C rates showed much faster capacity fade rates upon cycling, indicating significant degradation issues of the active material in simple aqueous electrolytes (e.g. Na_2SO_4(aq.)) and the need for new strategies to mitigate these issues in aqueous batteries.

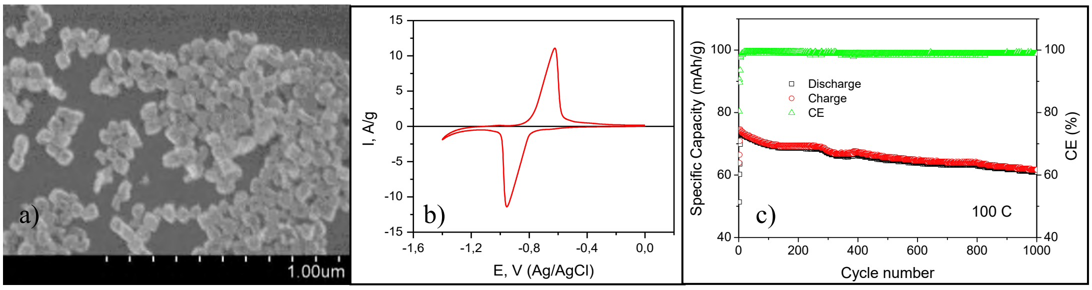

Fig. 1. a) SEM micrograph of nanostructured $NaTi_2(PO_4)_3$, b) cyclic voltammogram at 5 mV/s, c) charge/discharge capacity and Coulombic efficiency of nanostructured $NaTi_2(PO_4)$ during galvanostatic cycling at 100 C rate in 1 M Na_2SO_4

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Towards Reliable High-Temperature Electrochemical Devices: Proton Conducting Ceramic Cells in Metal Supported Architecture

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Electrochemical energy conversion from renewable resources offers promising routes to alternative energy resources, as well as to significant reduction of CO_2 emission. For their functionality at high temperatures and high stability of the components, solid oxide cells (SOC) demonstrate many potential applications, e.g. fuel cells and Power-to-X (P2X) technologies, of high efficiency and durability for long term operation. P2X technologies cover various processes converting electric energy into heat, hydrogen or synthetic fuels, while reducing CO_2 emission and providing huge capacity of energy storage. Proton conducting ceramic cells (PCC) were developed and their potentials for fuel cells and P2X applications were reported decades ago. The PCC geometry allows to supply and to produce pure hydrogen in fuel cell and steam electrolysis operations, respectively, which prevents fuel dilution and maintains P_{H_2O} low in Ni-based fuel electrode, in contrast to conventional SOCs. PCCs are also promising in the application of hydrogen extraction, pumping and compression as well as direct synthesis of hydrocarbons. However, the refractory character of the PCC electrolytes restricts upscaling of cell size and the manufacturing yield, and reliable air electrode materials are not yet well identified to realize highly efficient and reliable PCCs. In contrast to ceramic supported cells, metal supported (MS) architecture offers intrinsically superior mechanical strength, tolerance under thermal/re-dox cycles and cost reduction by replacing expensive ceramic based supporting materials with cheap metal alloys. One of the specific challenges is to find a process for the manufacturing of gas-tight electrolyte layers below 1000 °C that MS can withstand.

Transferring the know-how and technologies developed on MS-SOCs with thin film electrolyte [1], here we report our development of MS-PCC in the project DAICHI (EIG CONCERT-Japan): Thin and dense electrolyte coatings of $BaZrCeO_3$-based perovskites were successfully fabricated by pulsed laser deposition (PLD) technique implementing macro-/mesoporous electrode layers laminated onto ITM supports – commercial porous metallic substrate – having pore size of a few tens of µm [2]. Latest status of the MS-PCC development will be presented and prospects and challenges will be discussed towards the manufacturing of robust, durable, efficient and cost-effective MS-PCCs.

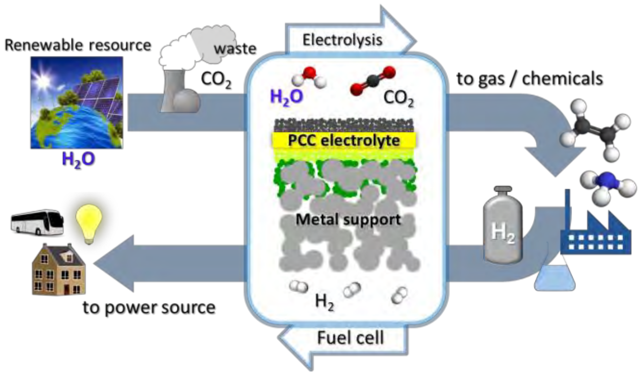

Figure 1. Electrochemical energy conversion via proton conducting ceramic cells, from renewable resources to gas and chemicals, and to power source.

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Functionalisation of Carbon Blacks by Nitrogen Plasma Treatment for PEMFC Applications

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Proton exchange membrane fuel cells (PEMFC) are widely considered as an effective means of reducing the carbon footprint of transport. PEMFC electrodes commonly comprise a carbon support on which a platinum catalyst is deposited, an ionomer and gas diffusion media, collectively ensuring the transfer of reactants, electrons and protons. Although the reaction is kinetically slow, carbon is thermodynamically unstable under PEMFC operating conditions, and oxidation of the carbon support leads to aggregation and/or electrical insulation of platinum, increased hydrophilicity, and a decrease of fuel cell performance.
The main goal of this work is to increase the durability and the activity of the PEMFC cathode[1 2]. With the aim of modifying the carbon support to improve its corrosion resistance and its interaction with catalyst and ionomer, carbon blacks were functionalised by a nitrogen plasma treatment. A range of carbon supports with different specific surface area and porosity were used to study the impact of their properties on the functionalisation.

Elemental analysis and X-ray photoelectron spectroscopy were performed to quantify and determine the chemical speciation of formed nitrogen functionalities (pyrrolic, pyridinic, *etc*…). The influence of the nitrogen plasma treatment on the morphology of carbon supports was observed by transmission electron microscopy (TEM, Fig. 1). The interaction strength between the carbon support and the ionomer was quantified by isothermal titration calorimetry[3]. The impact of the functionalisation on the stability of the carbon supports was studied by chronoamperometry at high potential giving access to their corrosion resistance.

By modifying the experimental conditions, carbon blacks with different nitrogen contents were obtained in a controlled way, allowing a relationship to be established between the level of functionalisation and the properties relevant for their application as catalyst support in PEMFC cathodes.

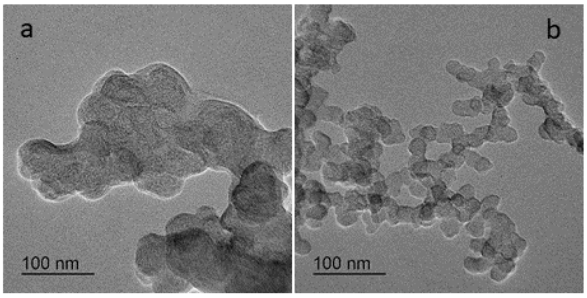

Figure 1: TEM images of carbon black Vulcan XC72R before (a) and after nitrogen plasma treatment (b)

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Demonstration of the novel imaging system based on bipolar electrochemistry for high spatio-temporal resolution bioimaging

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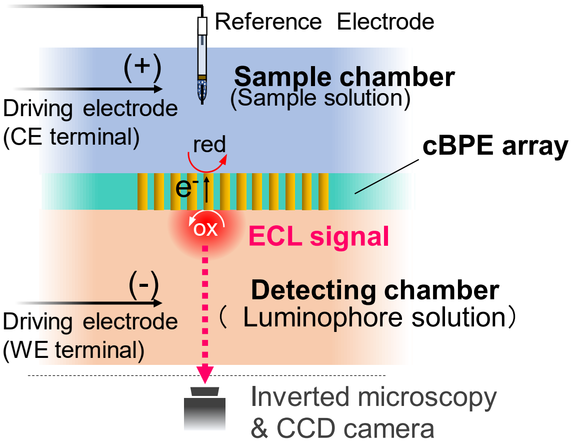

Fig. 1 Schematic of BEMs

Electrochemical imaging based on amperometric detection using multi-electrode array has been used for various biological sample observations such as metabolic activity of cell spheroids, and a neurotransmitter release activity in a rat brain slice, with its advantages of high sensitivity, high temporal resolution, label free feature. However, conventional multi-electrode arrays require the presence of connecting lines between the voltage supplier and individual electrodes, which severely limits the spatial resolution of the resulting electrochemical images. Therefore, the behavior of biomolecules associated with some biological phenomena which occurs in small area couldn't be observed with conventional multi-electrode array method. To overcome this problem, we have developed "Bipolar electrochemical microscopy (BEMs)" for high spatio-temporal resolution imaging of biological molecules. The BEMs employs closed bipolar electrode (cBPE) with electrochemiluminescence (ECL) detecting system as a pixel unit of images. Due to the feature that each cBPE need no connecting lines, high density cBPE array can be realized, and high spatio-temporal resolution imaging of target molecules using ECL signals can be realized.

Figure 1 shows the schematic of cBPE imaging system. Two driving electrodes (Counter electrode, reference electrode, working electrode) were inserted to the sample chamber and the detecting chamber. By applying a driving voltage, reduction reaction of sample molecule and oxidation reaction of the luminophore molecules occurs simultaneously, therefore, ECL signal generates on the surface of the cBPEs in the detecting chamber.

To monitor the MCF-7 respiration activity, living MCF-7 spheroid and a dead MCF-7 spheroid treated with paraformaldehyde was put on a cBPE array. Driving voltage was applied while observing the ECL signal by CCD camera. As a result, a larger ECL signal decrease was observed at the position where the live cell spheroid was placed. The results indicate that the cBPE imaging system can be applied in the observation of biological activities (Figure 2).

In future, various biological phenomena will be observed by enhancing the target molecules by using enzyme modification on cBPE array. Moreover, higher spatial resolution imaging will be realized by fabricating higher density cBPE array.

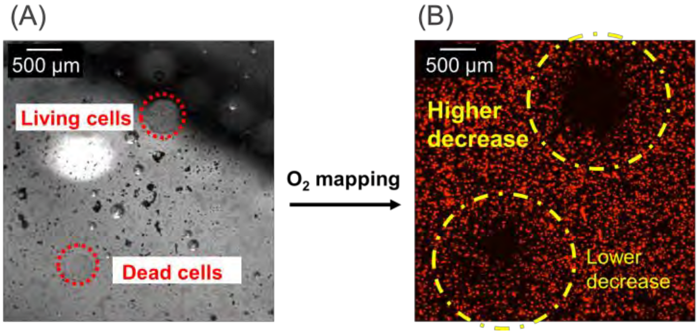

Fig. 2 (A) The living/dead cell spheroids placed on the surface of cBPE array, (B) ECL image observed while applying the O_2 mapping voltage.

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Lithium Interphase Enhancement for Lithium Sulfur Batteries

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Achieving stable dendrite-free and corrosion-free lithium metal anode is regarded as the utmost challenge in battery applications. Dendrite formation stemming from the non-uniform plating of Li during the battery charge will eventually perforate the separator and will internally short circuit the battery causing serious safety concerns. Besides, lithium metal is intrinsically very reactive and can easily react with the electrolyte and lithium salt, and thus solid electrolyte interphase (SEI) will be formed on its surface that is an unstable layer and leads to a substantial capacity loss. Moreover, regarding lithium-sulfur (Li-S) batteries, the migration of the soluble polysulfides through the separator towards the anode (polysulfide shuttling) and the subsequent reaction with the lithium will complicate the SEI composition and hinders a stable SEI formation.

To circumvent the abovementioned issues, several approaches have been investigated through designing lithium interphase via electrolyte additives or artificial SEI, designing lithium metal hosts with and without pre-stored lithium as well as any hybrid solutions.[1]

Herein, we have initially examined the role of the electrolyte additive in tuning the SEI formation by applying $LiNO_3$ as one of the most promising and widely used additives in two different concentrations. The comparison of the overpotiential profiles of the Li//Li symmetric cells during galvanostatic cycling showed that symmetric cells with concentrated $LiNO_3$ electrolytes demonstrated very small and relatively smooth overpotential profiles suggesting that $LiNO_3$ at higher concentration is beneficial to have stable interphase between Li metal and the electrolyte. With the aim of suppressing the formation of the lithium dendrites and achieving prolonged cycling, the study was further broadened to fabricate ex-situ protective layers on lithium anode. The attention was given to choose artificial layers that are mechanically and chemically stable, possess simple fabrication methods, and are preferably lithium ion conductors. Considering these criteria, Poly-dimethylsiloxane (PDMS) and Li_3N were chosen as artificial layers of interests [2,3]. A facile, economical synthesis method is proposed to fabricate each modified lithium anode. The electrochemical behaviors of the modified electrodes in terms of galvanostatic cycling performance and electrochemical impedance spectroscopy were probed in both symmetric configurations and later as anodes in Li-S cells. In-situ dilatometry can be adopted to investigate the volumetric fluctuations of the Li-S cells with pristine and modified anodes during the charge/discharge cycles.

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Investigation of structural changes in different metal ion battery electrodes by in-situ dilatometry

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Metal ion batteries are the most familiar energy storage figured for consumer electronics, portable devices, and electric vehicles. Accordingly, it is fundamental to improve their safety, to prevent failures and damages as well as to increase energy density and reduce the production costs. To understand the structural properties of electrodes materials during the battery operation and simulate their ageing are trivial steps to let a reliable battery functioning. The insertion/deinsertion of metal ions in the battery electrode's lattice leads to structural changes and expansions/shrinking that can limit the performance of the battery. [1, 2]

Between the different approaches useable for studying these volume changes, electrochemical dilatometry enables us to deliver versatile information about macroscopic in-situ expansions helpful for material design, details about SEI formation and irreversible/reversible components of dilatation which can be used to predict the long term stability. [3]

The present study aims to take this information into three typologies of batteries using various operating conditions such as use sundry electrochemical techniques and different applied forces. The thickness changes were investigated in lithium ion, sodium ion, and lithium sulfur systems during galvanostatic charge-discharge as well as cyclic voltammetry. Recording the dynamic behavior of the thickness change over several cycles was possible to consider the eventual structural instability during the operation of the systems investigated and dimensional change mechanisms.

Acknowledgements:
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Functionalization of Titanium Surface by Innovative Anticorrosion Coating

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Since implantation success strongly depends on the osseointegration process, current trends in dental implant research are based on surface properties modifications by biomimetic and bioactive coatings that mimic biochemical surroundings and architecture of the human bone. Calcium phosphate ceramics, like hydroxyapatite, with mineral composition similar to natural bone, as a single compound coating or as a composite with collagen, bioglass, or silica are used to promote osseointegration or overall implant system's characteristics [1]. Drug-based coatings with bisphosphonates like Zolendronate or Alendronate, drugs for bone diseases, promote mechanical fixation of implant and bone mineralization[2].

However, it must not be forgotten that a fundamental prerequisite for the success of osseointegration is a long-term corrosion stability of implant materials. Human body fluids, especially oral cavity fluids, in which pH is constantly changing, represent very aggressive media with high concentrations of chloride ions that are among the most aggressive and corrosive to metals. Although titanium is a gold standard in dental implantology due to its exceptional biocompatibility and corrosion resistivity, there is an increasing data reported regarding complications caused by titanium dental implant fixation. It was shown that titanium ions, that originated as product from corrosion reaction in body fluids, caused negative immune reactions or skin allergies immediately or shortly after implant fixation [3]. Therefore, it is crucial to design a coating which will make titanium surface more bioactive/osseoinductive and at the same time more corrosion resistant during a long-term exposure to oral cavity fluids.

In this study the titanium surface was modified by vitamin D3, molecules that are crucial for maintaining bone mineral density and normal functioning of the immune system [4]. The main goals were (i) to improve titanium corrosion resistivity during exposure to an artificial saliva solution and simultaneously (ii) to induce *in vitro* processes of "new bone" formation. According to results of all techniques, the D3 vitamin layer imparted very good corrosion protection to the oxide-covered titanium and induced a formation of biocompatible bone-like calcium phosphates what confirmed enhanced titanium's bioactivity level.

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Styrene-ethylene-butylene-styrene (SEBS) Copolymer Based Alkaline Anion Exchange Membrane with Piperidine Cross-linking reagents

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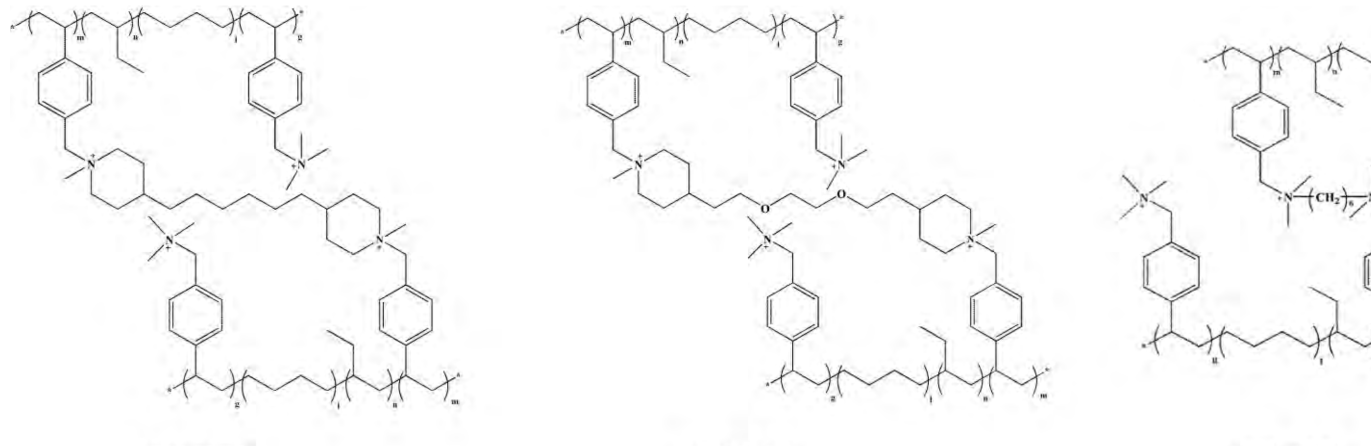
There is a paramount importance for us to develop a cost-effective electrolysis technology for green hydrogen in power supply system. On this point, polymer electrolyte membrane (PEM) electrolysis stands out due to its compactness and high efficiency and Alkaline exchange membrane with non-precious catalyst becomes a future primary choice. Herein we develop a novel alkaline anion exchange membrane with SEBS as the backbone and piperidine based diamine as the cross-linking agents. In detail, first Membrane with mutication crosslinking structure has better conductivity than and replace the quaternary ammonium with quaternary piperidine groups can increase membrane's chemical stability. Then, adding oxygen in the crosslinking structure can further increase its conductivity and 6 carbon between functional group has relatively balanced conductivity and chemical stability. Finally, SEBS-P2O6 has a conductivity of 20.8mS/cm (OH-) at room temperature, which is much higher than SEBS piperidine membrane published before.

m	**Conductivity (mS/cm)**	**Conductivity (mS/cm)**	**IECa**	**IECb**
	Cl$^-$ form 100% humidity	**OH$^-$ form 100% humidity**		
SEBS-N2C6	**5.66**	**10.2**	**0.96**	**0.44**
SEBS-P2C6	**6.45**	**12.5**	**1.05**	**0.40**
SEBS-P206	**11.7**	**20.8**	**1.10**	**0.42**

Table 1. Conductivity on SEBS-P2C6-TMA, SEBS-P2O6-TMA and SEBS-N2C6



SEBS-P2C6 **SEBS-P2O6** **SEBS-N2C6**

Fig 1. Structure of SEBS-P2C6, SEBS-P2O6 and SEBS-N2C6

Electrical Properties of molten TiO_2 – SiO_2 – Al_2O_3 – MgO – CaO slag

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The use of molten oxide electrolysis to produce metals has been proven more sustainable and environmentally friendly than most common traditional metallurgical processes. The potential to reduce emissions to the environment increases if large-scale waste materials are to be used as feedstock for this process. Previous work has shown that the electrochemical recovery of metals from the molten TiO_2 – SiO_2 – Al_2O_3 – MgO – CaO slag, a by-product of the ironmaking process, is feasible. However, a more extensive understanding of the electrochemical behaviour of this complex oxide system in its molten state is paramount in the design of industrial electrolytic cells. In this work, we study the effect of the experimental processing conditions, such as atmosphere, electrode material and electrolyte composition, on the electrical properties of the slag, crucial information to foster its recycling.

Electrochemical Dealloying as a Tool to Tune Composition, Porosity and Catalytic Activity of Nanoparticles

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Electrochemically dealloyed nanoparticles have been the focus of electrocatalyst research work for more than a decade. This research ranges from fundamental understanding of the dealloying processes[1] to practically relevant materials that show highly increased catalytic activity for important reactions like the methanol oxidation reaction[2]. Despite all these research efforts, general guidelines what to look for during dealloying and how to properly tune a dealloying process to receive the best results, are lacking up until now.

Our work investigates in detail how different numbers of cycles influence the resulting morphology, composition and catalytic properties, using cyclic voltammetry (CV). Using AgAu nanoparticles as an easy to understand bimetallic system[3] and the hydrogen reduction reaction (HER) as an example reaction, we reveal the existence of an optimal amount of cycles and how it can be easily spotted in a dealloying CV. When the CV gets featureless and does not change in the consecutive cycles, then the highest catalytic activity was found. Interestingly, complimentary identical location electron microscopy analysis showed that at this point the particles did not show the highest porosity. Longer cycling increased the porosity found in the particles, but decreased the overall catalytic activity, which indicates that higher porosity in nanoparticles does not necessarily lead to a higher catalytic activity.

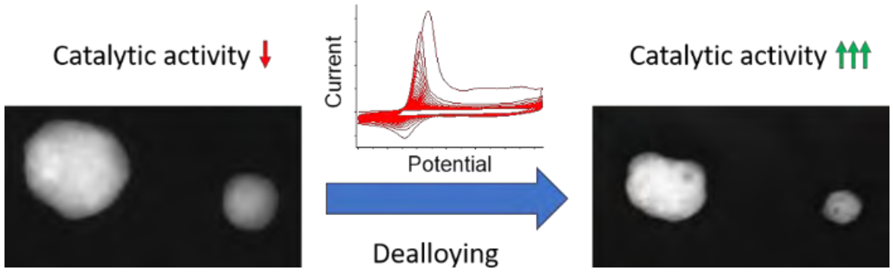

Figure 1. Schematic representation of electrochemical dealloying.

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Tracking Structural Changes using Electrocatalytic Reactions – HER on Au(111) during Potential-Induced Reconstruction

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Au(111) is one of the extensively studied single crystals. Its surface is able to reconstruct not only in UHV but also in electrochemical environment [1]. The phase transitions between the reconstructed and unreconstructed electrode surfaces have mostly been investigated by means of *in-situ* scanning tunneling microscopy, which revealed the existence of a variety of potential-dependent morphologies [2]. Kinetic studies are sparse and in the case of potential-induced reconstruction limited to *in-situ* surface x-ray scattering [3]. Classical electrochemical methods such as cyclic voltammetry can provide structural information of the electro-neutral reconstruction in an indirect way by considering changes in the signals of anion adsorption processes. Since, the electrocatalytic hydrogen evolution reaction (HER) on gold electrodes is strongly structure-sensitive [4], it is used in this study to monitor structural changes of the Au(111) surface. The electrocatalytic activity is highest at $t = 0$, directly after the surface reconstruction had been lifted, and decreases while the potential-induced reconstruction proceeds, following a simple first-order rate law (Figure 1a). In contrast to expectations from conventional electrode kinetics, the rate of the reconstruction process is decreased with more negative potential, as the reconstructed surface is stabilized by increasing negative excess charge. The observed trend can further be explained by a change in bond strength between Au surface atoms, as indicated by a potential-dependent compression of the topmost Au layer [5]. The systematic investigation clearly exhibits an exponential potential-dependence of the rate constant if specific adsorption is avoided. Temperature-dependent measurements at -0.4 V yield an apparent activation energy of ~0.6 eV. The adsorption of anions slows down surface reconstruction (Figure 1b), while the adsorption of carbon monoxide leads to an enormous enhancement of the reconstruction rate.

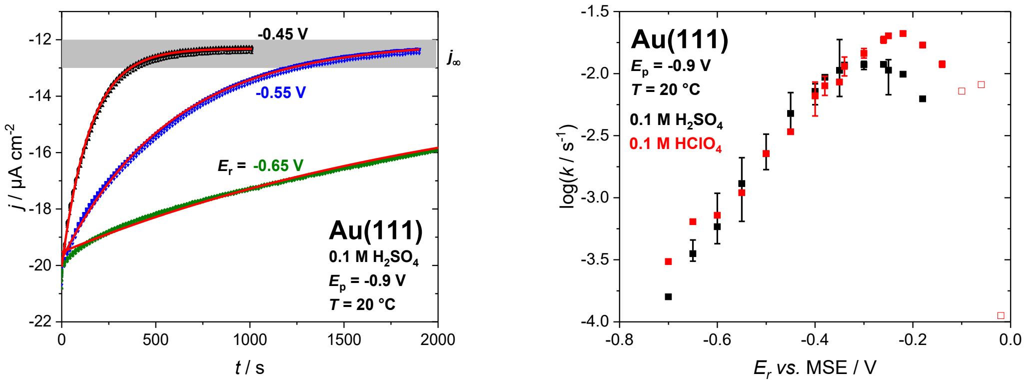

Figure 1: (a) Current density-time curves of HER at Au(111) in 0.1 M H_2SO_4 at probing potential E_p = -0.9 V and 20 °C for different reconstruction potentials, E_r = -0.45 V (black), E_r = -0.55 V (blue), and E_r = -0.65 V (green). Corresponding exponential fits are depicted in red. The range for stationary current density j_∞ derived from the fitted curves is indicated in gray. (b) Logarithm log(k / s^{-1}) of average rate constants extracted from exponential fits *vs.* reconstruction potential for Au(111) in 0.1 M H_2SO_4 (black) and 0.1 M $HClO_4$ (red). Error bars indicate scattering of different measurements.

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Reduced Graphene Oxide as an Advanced Supporting Material for Pt-based ORR Electrocatalysts in PEM Fuel Cell Applications

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Proton exchange membrane fuel cells (PEMFCs) have attracted wide attention due to their high energy efficiency and zero harmful emissions. However, providing high catalytic activity and long-term stability of the electrocatalyst remains a challenge. Currently, the most common oxygen reduction reaction (ORR) electrocatalysts are based on Pt or Pt-alloy nanoparticles (NPs) supported on high surface area carbons (commercially available carbon blacks such as Ketjen Black EC300J or Vulcan XC72) [1]. Despite many inherent good properties of carbon black supports (*e.g.* low cost, high conductivity, high surface area, etc.), poor electrochemical stability (*i.e.* carbon corrosion) as well as sub-optimal Pt utilization (*i.e.* nano-porosity) hinder performance under operational conditions of the PEMFC. Carbon corrosion results in secondary degradation mechanisms such as agglomeration of Pt/Pt-alloy NPs or their detachment which both consequently lower the active Pt surface area. On the other hand, Pt/Pt-alloy NPs located in nano-pores of carbon blacks are known to not efficiently contribute to the electrocatalyst performance at high current densities. This is due to their sub-optimal three-phase boundary as a consequence of poor ionomer coverage and accessibility for reactants and products. Past studies have revealed that many properties of the carbon support such as degree of graphitization, surface area, porosity type and size, functional groups etc., play a key role on both the aspects of carbon corrosion as well as Pt utilization [2].

This work is, thus, focusing on improving the properties of the supporting material by exchanging conventional carbon blacks with graphene-based materials. Graphene oxide with different degrees of oxidation, graphitic particle size and functional groups was used as precursor for preparation of various reduced graphene oxide supports (rGOs) that were decorated with nanoparticles of less noble metals (namely Cu and Ni). Using our in-house developed double passivation with galvanic displacement method [3], Pt-alloy nanoparticles were prepared on different types of rGO supports. Various structural and electrochemical analysis methods were performed for comparison of the Pt-alloy/rGO electrocatalysts. This includes X-Ray diffraction (XRD), scanning electron microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), Brunauer–Emmett–Teller (BET) specific surface area, Raman spectroscopy and elemental analysis for structural analysis as well as half-cell TF-RDE (ORR and CO electrooxidation) and a proprietary high temperature disk electrode (HT-DE) for electrochemical analysis. Specifically HT-DE was used to gain insight into the electrochemically induced carbon corrosion at an elevated temperature (60 °C - temperatures more relevant to operation of PEMFCs) by comparing Pt surface area degradation of different rGOs and carbon blacks.

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Insights into the formation and composition of the SEI on carbon-coated TiO_2 electrodes for Na-ion batteries by depth-dependent X-ray photoelectron spectroscopy

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The continuously growing demand of lithium ion batteries (LIBs) for portable electronics and in the rapidly increasing sector of electric vehicles raises concerns about the long term availability of critical raw materials employed in the LIB industry, such as lithium, cobalt, graphite and copper [1]. Owing to their potential lower cost and higher sustainability compared to the current lithium-based technology, SIBs have the potential to dominate the future stationary storage market. Among the anode materials proposed for SIB application, easy-to-synthesize TiO_2 nanoparticles exhibit promising properties especially in terms of high reversible delivered capacity and excellence cyclability [2,3], however the understanding of the processes occurring at the electrode/electrolyte interfaces (EEIs) and their degradation modes is still incomplete.

It is evident that the EEIs in SIBs play a key role, indeed, the successful design of well-performing SIBs relies in the stabilization of the interfaces governing these complex systems. The formation and evolution of the solid electrolyte interphase (SEI) layer as well as its morphology, chemical composition, and stability significantly influence the cell lifetime and performance.

Due to its high chemical sensitivity and tunable penetration depth, photoelectron spectroscopy is a powerful technique for the investigation of the chemical composition and in-depth profile of the SEI layer. In particular, hard X-ray photoelectron spectroscopy (HAXPES) allows probing the relevant near-surface region including the SEI/anode interface. HAXPES thus enables the differentiation of the components of the SEI from those related to the Na^+ uptake in the electrode.

In order to gain more insights on the formation of the SEI on a high-performance carbon-coated TiO_2-based SIBs anode, electrode samples at different stages of (dis)charge have been investigated with 2 different excitation energies (i.e. different probing depths) in the HiKE endstation [3] at the BESSY II KMC-1 beamline [4] at HZB. A detailed evaluation of the core-level spectra associated with the electrode, reveal the formation of a stable SEI layer partially composed of polyethylene oxide, sodium alkyl carbonates, sodium alkoxides, and minor contributions from sodium fluoride and sodium chloride derived from salt, binder and carbonate-based electrolyte decomposition. In addition to the formation of a polyolefin-based layer between the electrode surface and the SEI during the first cycle, the appearance of an accumulation layer could be detected, which could account for the charge neutrality of the system in highly sodiated states of the electrode and which induces an observable downward band bending. By considering the different inelastic mean free paths (IMFP) used in the experiment, the thickness of the SEI on the C-TiO_2-based electrode as well as the change of the Ti oxidation state due to Na^+ insertion in the discharging process has been estimated. The results provide comprehensive insights into the SEI formation and composition on C-TiO_2-based anodes used in SIBs, representing a useful dataset toward a better understanding of the complex nature of the interfacial processes occurring in SIBs.

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Sodium insertion into TiO_2 electrodes during (dis)charging of sodium-ion batteries monitored by *operando* XANES

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The sodium ion battery (SIB) technology has the potential to represent a readily available, cheaper, and more environmentally friendly alternative electrochemical energy storage system to the most widely adopted lithium ion batteries, especially for stationary energy storage application filling the gap between clean energy produced by renewable sources and its utilization. In order to meet the requirements for practical applications, research on improved electrode materials is necessary. Recently, the excellent performance of a TiO_2 nanoparticles (np-TiO_2) anode for application in SIBs has been reported [1,2]. TiO_2 is certainly an attractive candidate, especially in terms of sustainability, cost and promising electrochemical performance. Nonetheless, the Na uptake and release mechanism is still heavily debated as well as a comprehensive understanding of the process occurring upon sodiation [2].

In particular, one of the main challenges is to unravel the structural and electronic changes of the anatase TiO_2 nanoparticles and the loss of crystallinity of the anodic nanomaterial upon Na uptake.

In this work, X-ray absorption near edge spectroscopy (XANES) at the Ti *K*-edge is used to investigate the electronic and geometric structure around the Ti atom and its nearest neighbors, allowing the identification of the sodiation effects on the TiO_2-based electrode. To gain direct, relevant insights into the insertion process of Na into the anatase-TiO_2 nanoparticle anode material, we designed an *operando* XANES experiment using a modified coin cell equipped with an X-ray transparent Kapton® window and a 6 µm-thick Al foil current collector adapted for the HiKE endstation [3] at the BESSY II KMC-1 beamline [4] at HZB. This setup allowed the measurement of the highly sensitive Ti *K*-edge of the np-TiO_2–based anode upon cycling, i.e. (de-)sodiating the electrode.

The analysis of the Ti *K*-edge absorption reveals a change in the average oxidation state of Ti upon sodiation from Ti^{+4} in the original anatase structure to around +3.4 (i.e. 0.6 Na atoms per unit formula). The *operando* results show that the oxidation state increases upon desodiation but does not reach the original Ti^{+4}, which is attributed to the presence of irreversibly trapped Na (~0.2 Na atoms), most likely responsible for the permanent loss of crystallinity in the nanoparticles observed during the first cycle. The analysis of the evolution of the pre-edge structure of the Ti *K*-edge, which is highly sensitive to coordination and oxidation, reveals that upon sodiation the pre-peak changes from the four-peak feature typical of the anatase structure [5] to a structure dominated by a single peak, suggesting a change in the number of nearest neighbors around the probed Ti atoms (from 6 to 5 neighbors) [6]. The subsequent cycling shows the same spectroscopic trends in the pre-edge feature, revealing a stable Na^+ uptake process after the initial irreversible structural rearrangement of the TiO_2 during the first sodiation process. The analysis performed enables an identification of the structural changes upon (de)sodiation of the np-TiO_2–based anode, which is crucial for a further insight-driven optimization of the electrode material.

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Ir-Nanoparticles Decorated TiO_2 Nanotube Arrays: Boosting the Hydrogen Evolution Activity through Morphological and Synergistic Effects

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Ultrapure hydrogen fuel produced by water electrolysis using renewable electricity from photovoltaic modules or wind turbines is seen as a viable future solution to alleviate the growing energy and environmental concerns of the modern world. The platinum group metals (PGMs) are unparalleled electrocatalytic materials for the cathodic hydrogen evolution reaction (HER) in terms of activity and chemical stability in acidic environments. However, their scarcity and expensiveness impede further development of the water electrolysis systems, so more cost-effective PGM-based electrocatalyst designs are in demand to bring the hydrogen economy concept closer to reality. Herein, we introduce a galvanic displacement strategy to decorate self-standing, protonated TiO_2 nanotube (H-TNT) arrays with ultrafine Ir nanoparticles. The procedure is based on a galvanic displacement-type reaction between the Ir(III) ions in $IrCl_3$ solutions and the H-TNTs serving as reducing agents. We demonstrate that a controlled morphological change from neat open-top tubes to disordered nanostripe bundles ("nanograss") during the step of anodic formation of TNT supports is beneficial for providing an abundance of exposed Ir active sites at the final self-standing Ir@TNT composites. Combined experimental evidence and computational modeling show that the nanograss H-TNT structures act as conductive supports that optimize the hydrogen adsorption energy of the firmly anchored Ir and regenerate its active sites during the HER, thus enabling the obtained Ir@TNT composite electrocatalysts to deliver an amazing HER performance. With only 5.7 μg_{Ir} cm^{-2} in the optimum Ir@TNT, we achieve an overpotential of –63 mV at –100 mA cm^{-2}, a low Tafel slope of –36 mV dec^{-1}, a mass activity of 34 A $mg^{-1}{}_{Ir}$ at –80 mV and superior durability in 1 M $HClO_4$. Moreover, the Ir@TNT catalytic structures outperform commercial Pt/C and Ir/C as well as most state-of-the-art PGM catalysts at high current densities. This work highlights the great perspective for the application of H-TNT arrays in HER electrocatalysis.

Nanosecond laser fabricated monolayer of gold nanoparticles on ITO for bioelectrocatalysis

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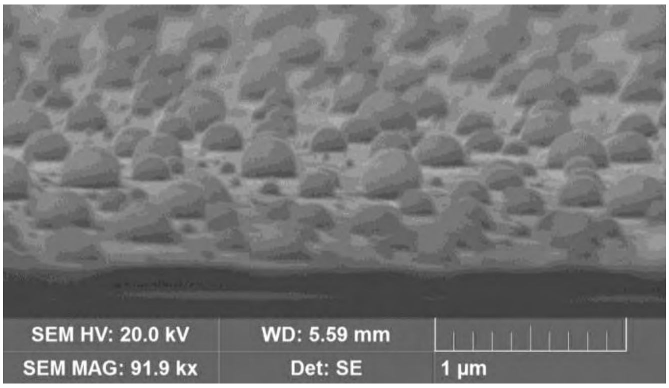
Redox enzymes can be envisioned as biocatalysts in various electrocatalytic-based devices. Electrode nanostructuration allowed enhanced loading of biocatalysts, hence higher current output. However, a weak percentage of loaded enzyme is operating, increasing the costs linked to enzyme production. Enhanced electron transfers were obtained by controlling key parameters for efficient immobilization. However, stability is limited to days in most cases (1-3). Among factors that play roles in these two limitations, the effect of enzyme-enzyme neighboring interaction on electrocatalysis has rarely been investigated, although critical *in vivo* (4).

Gold nanoparticles prepared by laser ablation may be a way for determining the relationship between activity and enzyme density on electrodes (5-6). We report in this work nanosecond laser interaction with nanometric gold films deposited on indium tin oxide support to generate in-situ AuNPs free from any stabilizers. A comprehensive analysis of AuNP size and coverage, as well as total geometric surface versus electroactive surface is provided as a function of the thickness of the treated gold layer. Using microscopy and electrochemistry, the long-term stability of AuNP-based electrodes in the atmosphere and in the electrolyte is demonstrated. AuNPs formed by laser treatment are then modified by thiol chemistry and their electrochemical behavior is tested with a redox probe. Finally, enzyme adsorption and bioelectrocatalysis are evaluated in the case of two enzymes, i.e. the *Myrothecium verrucaria* bilirubin oxidase and the *Thermus thermophilu*s laccase. Behaving differently on charged surfaces, they allow demonstrating the validity of laser treated AuNPs for bioelectrocatalysis.



SEM images of Au nanoparticles obtained from laser ablation of Au film on ITO.

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Revealing degradation and recovery mechanisms of Co_3O_4 nanocatalysts for oxygen evolution by *in situ* impedance analysis

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Co_3O_4 is one of the most active precious metal free electrocatalysts for the oxygen evolution reaction (OER).[1] Hence, extensive efforts have been made on studying its active sites.[2] In contrast, few investigations exist on its degradation mechanism and so comparably little is known about this important process. Herein, Co_3O_4 nanoparticles are used as OER catalysts under alkaline conditions and their degradation and re-activation are investigated by electrochemical studies linked to spectroscopy and high-resolution electron microscopy. A degraded activity is observed after chronopotentiometric catalyst ageing, which can be recovered by a simple experimental procedure. This behavior of the Co_3O_4 nanoparticles used in this study is further explained by extracting *in situ* information at different stages from electrochemical impedance spectra (EIS, Figure 1). By systematically varying experimental conditions, such as potential, catalysts' loading and pH, and by applying several EIS analysis methods, mechanistic insights into the OER catalysis mechanism of Co_3O_4 are gained.

Based on this, a feature appearing in the high-frequency region described by an RC element with increasing resistance and decreasing capacitance by several orders of magnitude, is identified as crucial for the catalyst deactivation. The corresponding structural changes are affected by the amount of OH^- available at the interface and the near-surface region of the cobalt oxide. Moreover, the evolution of the structural alteration with time and, hence, the decrease of OER performance during aging is influenced by this factor. This emphasizes the importance of solvation states and processes occurring during the linear sweep pre-OER wave. The easy-to-access *in situ* method of EIS is, highlighted as a powerful tool to analyze changes of electrocatalysts under working conditions and to shed light on the underlying catalysis mechanism.

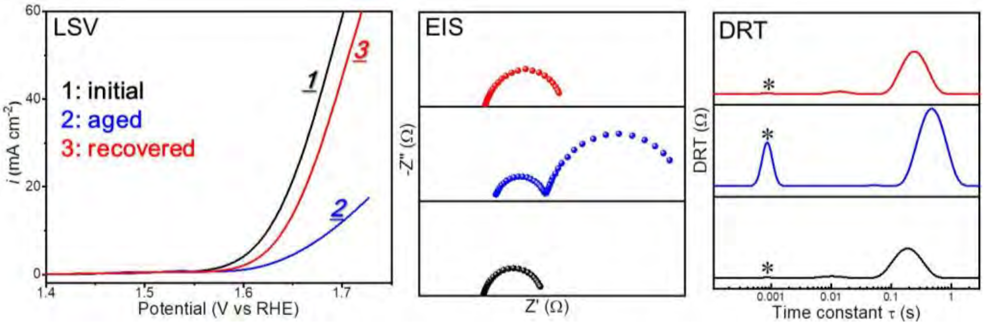

Figure 1. LSV, EIS and DRT graphs of Co_3O_4 nanoparticles in their initial, aged and recovered state.

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Organic Electrocatalytic Synthesis of Dimethyl Carbonate: Production, Analysis and Quantification

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Electrification is a potential solution to solving the challenges of the chemical industry, such as environmental pollution and use of petroleum as a starting material. Organic electrocatalysis offers a chance to perform cleaner chemical synthesis, ultimately with renewable energy and sustainable resources. In order to develop new synthesis routes, we ideally must first study and optimise reactions suitable for electrocatalysis. Dimethyl carbonate (DMC) is one candidate for investigation. DMC is a valuable chemical used on industrial scale for both production (e.g. carbonylation reactions) and in end products (e.g. paints and batteries). DMC is currently formed by thermal catalysis but can be formed electrocatalytically, it is a carbonylation product of methanol[1], formed electrochemically by the reaction $2CH_3OH + CO \rightarrow (CH_3O)_2CO + 2H^+ + 2e^-$.

The purpose of the work is to understand the fundamental aspects of the carbonylation reaction over an electrode surface, i.e. by heterogeneous electrocatalysis, rather than homogeneous or indirection electrosynthesis. Knowing the steps of formation and the reaction intermediates involved will allow us to develop the catalytic system in a rational manner as well as apply the knowledge to later reactions of interest (e.g. carbonylation of other alcohols, such as phenol, to form valuable products). Understanding the active site and mechanism of the reaction is paramount for rational optimisation strategies.

Different transition metals (Cu, Au, Pt) have been tested for their activity towards DMC production[1,2,3]. Au is more active than Pd in terms of current efficiency as well as current density (Figure 1), whereas Cu catalysis DMC synthesis via an inefficient solution phase mechanism. We have used different techniques to understand different aspects of the reaction and catalyst activity: in situ infrared spectroelectrochemistry (in situ FTIR) is used to study the interface and the reaction at relatively short timeframes while headspace gas chromatography mass spectrometry (HS-GC-MS) has allowed us to determine the selectivity and reaction efficiency, whilst learning about chemical steps that occur after electrolysis to the products in the solution. Detecting such reactions in solution are important for determine the catalyst mechanism of the end products. The results that we have obtained so far have been discussed in combination with a theoretical analysis which has helped us understand the mechanisms involved. Further development is underway for optimising the catalyst as well as reactor system.

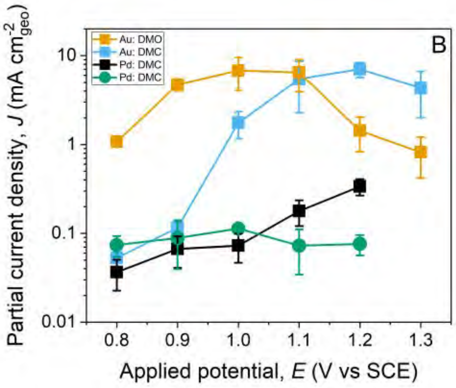

Figure 1. Partial current density for the formation of DMC and DMO on Au and Pd electrodes. 0.1 M NaClO4 in methanol saturated with CO, room temperature and atmospheric pressure.

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Mathematical modeling of PEM water electrolyser performance and degradation for different IrO_2 loadings

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The aim of present study is to investigate numerically an effect of the IrO_2 loading on anode onto proton-exchange membrane (PEM) water electrolyser (WE) performances. The rate of the IrO_2 dissolution depending on WE operation modes has been estimated as well.
Physicochemical model [1] was used as the basis for the calculations. Two-phase mass transport in current collectors/gas diffusion electrodes has been considered. Electrochemical reactions in catalytic layers associated with IrO_2 dissolution have been included in the developed mathematical model as well. The rate of anode dissolution of the IrO_2 was estimated depending on the anode overvoltage based on the results reported in [2, 3]. Figure 1 shows the cell voltage V and the rate of degradation of WE performances due to the anode dissolution of the supported and unsupported IrO_2.

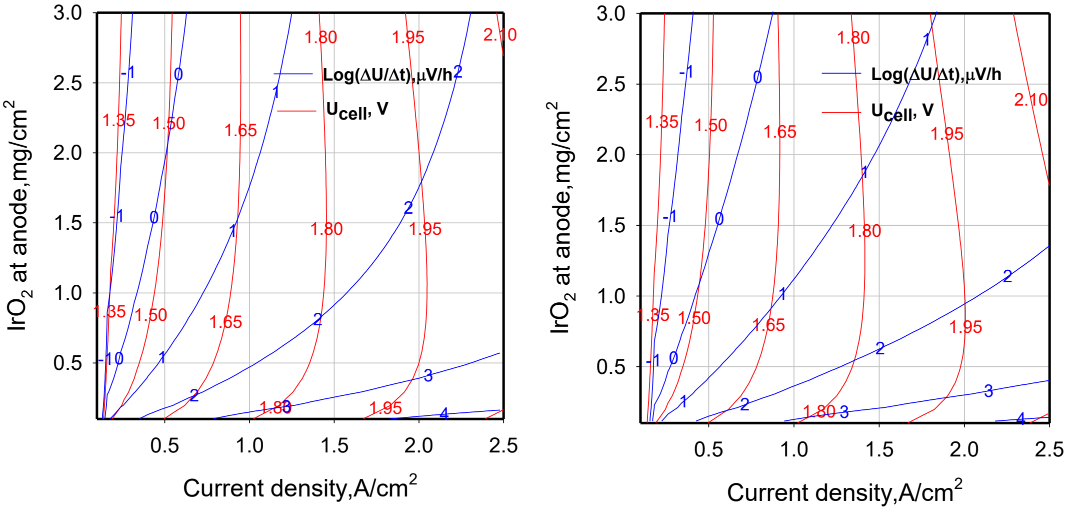

Figure 1. Dependence of WE voltage (U_{cell}) and it's degradation rate ($\log(\Delta U_{cell}/\Delta t)$ upon current density and IrO_2 loading in catalytic layer for the cases of unsupported (left) and TiO_2-supported IrO_2 (right).

The calculation data demonstrate good correlation with the experimental results [2, 3]. In particular, calculations show that the use of an ultra-low IrO_2 loading on the anode increases the rate of the performance degradation by a factor of 1-2. The use of the supported catalyst allows to reduce this degradation rate by 2-3 times. It should be noted that the degradation rates of PEM WE performances observed in experimental studies may be caused not only by the dissolution of the IrO_2. Therefore, the calculated degradation values may differ from those determined experimentally. The proposed numerical data allow to estimate the trend of performance degradation of WE at change of membrane-electrode assembly parameters.

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Composite PAAm-based hydrogel electrolyte for hybrid aqueous (Zn-Li-ion) battery

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Hybrid aqueous rechargeable batteries are very attractive alternative to conventional rechargeable lithium ion batteries for stationary application because of production and usage safety, reduced production cost and environmental friendliness. Previously aqueous rechargeable batteries with Zn/LiCl-$ZnCl_2$/$LiFePO_4$ system with liquid electrolyte has been reported [1]. The system performed a high rate capability up to 60 C with the average operation voltage 1.2 V and cycling performance with a capacity retention of 80 % over 400 cycles at 6 C.

However, there are several drawbacks including water decomposition and zinc dendrite formation hindering the commercialization [1]. The present study aimed to develop a PAAm-based hydrogel electrolyte with inclusion of montmorillonite and halloysite clay nanoparticles for hybrid aqueous rechargeable zinc/lithium ion batteries to overcome above mentioned problems. Polyacrylamide hydrogel was chosen because of its high ionic conductivity, high water content and simple fabrication method in which cross-linking degree, thickness, etc. were optimized. Inclusion of clay could improve mechanical stability of hydrogel electrolyte, prevent water decomposition and dendrite formation.

All tests performed in Zn/$LiFePO_4$ cell operating in an optimized LiCl/$ZnCl_2$ aqueous electrolyte based hydrogel.

Acknowledgement

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Amplification-free point-of-care microRNA detection in urine using molecular beacon based electrochemiluminescence

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The burgeoning field of miRNA detection using electrochemiluminescence (ECL) has garnered a great deal of attention in recent times.[1] ECL presents many advantages over alternative detection strategies as ECL analyses generally exhibit low-background signals, high sensitivity, are reproducible and scale-able.[2] When combined with magnetic-beads for the immobilisation of biological recognition elements, ECL biosensors offer exceptional sensitivity owing to the ability to disperse the beads in large sample volumes to capture the biological target of interest *via* mixing then concentrate prior to analysis *via* magnetic extraction.[3, 4]

Herein, we present a novel biosensor for the sensitive detection of miRNA-21 comprising a molecular beacon ECL probe immobilised on magnetic beads. We obtained a limit of detection of 500 attomoles for miRNA-21 without enzymatic amplification or the addition of detection probes or intercalating labels, negating the need for lengthy and stringent washing procedures to reduce the background signal. Furthermore, we demonstrate the immense potential for point-of-care applications by developing a fully integrated miRNA detection platform.

The platform comprises a portable-potentiostat for ECL generation, mobile phone for ECL detection and a custom 3D-printed cell holder to readily interface a disposable screen-printed electrode with the potentiostat and phone camera. When combined with point-of-care miRNA extraction methods, the molecular beacon based ECL system we have developed presents a promising tool for point-of-care diagnosis and management of numerous diseases.

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A Comprehensive Study on the Electro-catalytic Activity and Selectivity of Single-crystalline and Poly-crystalline Zirconium Nitride Thin Films Towards Nitrogen Electroreduction and Ammonia Synthesis

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The Haber-Bosch process which is currently responsible for the whole production of ammonia for nitrogen (N)-fertilizers, operates at high temperatures and pressures releasing around 1.6-3.8 tons of CO_2 per ton of NH_3 produced. The process also operates on a vast scale in a few locations worldwide, necessitating a network of transportation to deliver the final N-fertilizer to individual farmers. Thus, there is an unmet need for a distributed ammonia production process that can operate locally at a smaller scale under ambient conditions for a single farmer or a group of farmers. This study presents the steps towards the realization of this goal through the alternative of electrochemistry.

Electrocatalytic conversion of N_2 to NH_3 at ambient and semi-ambient conditions in an aqueous electrolyte, using a zirconium nitride catalyst – predicted by density functional theory (DFT) calculations –was comprehensively studied in batch-cell and flow-cell. The catalysts were deposited as thin films in various single-crystal structures with orientations of (111), (100), and (110) facets and polycrystalline thin films, using reactive magnetron sputtering. For each surface, two electrolytes were tested in an H-type batch-cell and depending on the cyclic voltammograms obtained in N_2 vs. Ar gas, the most promising electrolytes were tested further in a micro-reactor flow-cell which was connected in-line to an ammonia quantification unit. A new electrochemical pulsing methodology was developed to address persistent challenges associated with this electrochemical reaction, namely low current efficiencies and low reaction rates. The experiments aimed to understand the effects of the applied potential and its duration on the surface reactivity and stability for each of the ZrN facets. X-ray photoelectron spectroscopy (XPS) and X-ray reflectivity (XRR) analysis were carried out on pristine and used catalysts to study the surface changes throughout the electrochemical processes. Control experiments in Ar gas and isotope-labeling experiments were performed, as well, to investigate the source of ammonia produced. Presence of hydrazine and nitrate was ruled out as side-products. The results show significant differences between surface structure and applied potential for both reaction rates and current efficiency towards ammonia formation and indicate that surface engineering may help in designing more efficient catalysts for nitrogen reduction reaction (NRR).

Keywords: nitrogen reduction reaction; ammonia; electrocatalysis; electro-catalytic activity; electro-catalytic selectivity

Hybrid hydrogen-bromate redox flow battery as a rechargeable power source

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Flow batteries have recently become one of the most promising technologies in the field of large scale energy storage since they provide a possibility to adjust their power-to-energy ratio in the wide range with minimal expenses. In the search for novel types of such devices it was demonstrated [1] that it is possible to carry out the electroreduction of bromate anions in acidic solution on carbon electrodes due to the presence of bromine, even in trace amounts. In this case, an autocatalytic cycle consists of a heterogeneous reaction on the electrode surface for a reversible redox couple of Br_2/Br^- and an irreversible homogeneous reaction of the BrO_3^- and Br^- comproportionation into Br_2. Use of bromates as energy-intensive substances is a promising approach because it allows one to increase the energy density of flow batteries from tens to hundreds of W h/kg.

The main purpose of this study has been to investigate the whole process of electrooxidation of a bromide anion and then inverse electroreduction of the bromate anion in a testing cell with one membrane electrode assembly. Two modes of the cell operation were studied - for acidic and alkaline sodium bromide solutions. Also, different methods such as spectrophotometry and electrospray ionization-mass spectrometry (ESI-MS) were applied to control the composition of solution at the outlet of anodic compartment. It was found that after deep oxidation of acidified sodium bromide solution the resulting bromate-containing electrolyte might be successfully used ~~for~~ in combination with electrochemical hydrogen oxidation at anode inside the same electrochemical unit for the current generation, thus demonstrating for the first time the whole charge-discharge cycle of the hydrogen-bromate flow battery (Fig.1). Its energy efficiency exceeding 72% was achieved for the second redox cycle in the 5-cycle series. Among the reasons of capacity decay, the main role is played by degradation of porous carbon material ~~at positive side~~ of the positive electrode of the cell. Several strategies to overcome this drawback have been formulated.

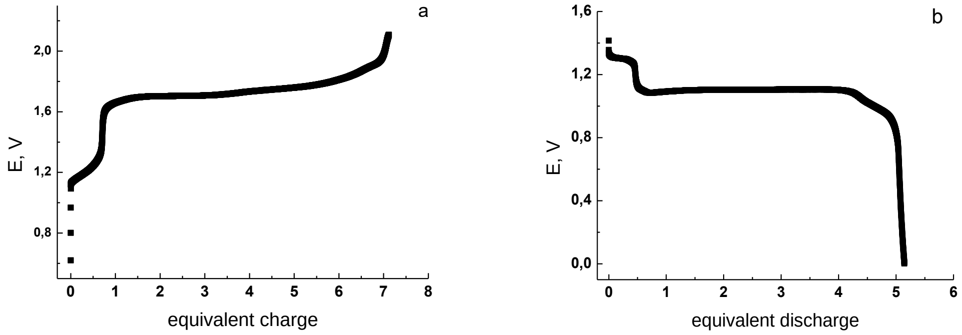

Figure 1 - Charge-discharge curves of H_2/BrO_3^- redox flow battery. Membrane electrode assembly design: positive electrode - Toray EC-TP1-120 carbon paper, negative electrode - Freudenberg H23C8 carbon paper (loading Pt / C 1 mg/cm^2), membrane - Nafion 117. a) galvanostatic mode:1 A, positive electrode - 0.5 M NaBr 1 M H_2SO_4, 50 ml/min, the negative electrode is open to the atmosphere, termination after passing 7 equivalents of the Br^-/Br_2 transformation charge; b) galvanostatic mode: -1 A, positive electrode -product of the stage (a), negative electrode - hydrogen, 10 ml / min.

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Sodium chlorate as catholyte in hybrid hydrogen-chlorate redox flow battery

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A promising direction of modern electrochemical energy science is redox flow batteries (RFB), which allow to generate and store electric energy as a result of electrochemical reactions of liquid reagents with high energy capacity - an oxidizing agent and a reducing agent. In the article [1] it was shown that it is possible to carry out the electroreduction of bromate anions in acidic media on catalytically weakly active electrodes (for example, carbon) via the redox mediator mechanism provided by the Br_2/Br^- redox couple. Later in the article [2], a hybrid chemical power source was demonstrated — a hydrogen-bromate redox flow battery using the cathodic reaction of the reduction of bromates in an acidic medium. In order to expand the range of oxidizing agents that are potentially prospective for chemical power sources of this type. We studied a flow cell with hydrogen gas oxidation at anode anв reduction of solutions of chlorates and their mixtures with bromates at cathode.

Positive electrode based on Toray TGPH 120 carbon paper and the negative one consisted of Pt / C catalyst with a Pt loading of 1.175 g/cm^2 spread on Sigraset 39AA gas diffusion layer were separated by Nafion 117 membrane. Hydrogen gas was supplied to the negative electrode, and 25 ml of an acidified solution of sodium halogenates of various compositions were pumped through the positive electrode in a cyclic mode. The current generated by the cell was measured at a constant voltage of 0.5 V (the OCP voltage was about 1.4V) until the oxidizer has been completely exhausted. The moment of complete conversion of catholyte solution was determined by the current approach to zero. It was found that for sulfuric acid concentration in the bromate-chlorate mixture below 1 M, the current generated by the cell is associated with the process of bromate reduction only, while chlorate acts as an indifferent additive. With ~~an~~ increase of the acid concentration over 3 M, the fraction of chlorate ions involved in the redox transformation increases and reaches unity at 6 M H_2SO_4. In addition, the use of oxidizing solution containing 6 M H_2SO_4 acid without addition of bromate results in a discharge current that flows after a certain induction period up to the complete reduction of chlorate to chloride. To study the processes occurring at cathode, we used the method of spectrophotometric analysis of the electrolyte at the outlet of cathode half-cell, which allowed us to determine the nature of the redox-mediator couple during reduction of the chlorate anion.

Acknowledgments. The reported study was funded by the Russian Science Foundation according to the research project № 20-63-46041.

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Electrochemical study of anatase TiO_2 nanotube arrays electrode in low viscosity ionic liquid electrolyte

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Ionic liquids (ILs), room temperature molten salts, can be considered as electrolytes for next generation of lithium-ion batteries (LIBs), because of their low flammability, thermal stability, good conductivity and wide electrochemical stability window. In order to decrease viscosity and further increase conductivity ILs are usually combined with some organic solvent (cosolvent) for LIBs applications[1,2]. In this work the 0.5 M solution of LiTFSI salt in low viscosity ionic liquid 1,3-diethylimidazolium *bis*(trifluoromethylsulfonyl)imide, (C_2C_2imTFSI), without cosolvent, was tested as electrolyte for LIBs by using robust anatase TiO_2 nanotube arrays (NTAs) electrode. The galvanostatic (GS) testing was performed at different current rates and also at different temperatures, 25-55°C, at current rate 3C, Fig. 1. Capacity of TiO_2 NTAs is due to both bulk and surface storage of Li^+-ion, and significantly increases with temperature increase. GS experiments demonstrated excellent capacity retention with improved Coulombic efficiency during final cycling at current rate ~3 C, but with the decrease in capacity of TiO_2 NTAs comparing to values before temperature raise or change of current rate[3]. The decomposition of electrolyte was observed by detecting the change of colour of electrolyte in bottle type cell during experiments at elevated temperatures. The formation of film on electrode surface and its increase after GS cycling at elevated temperatures was confirmed by electrochemical impedance spectroscopy.

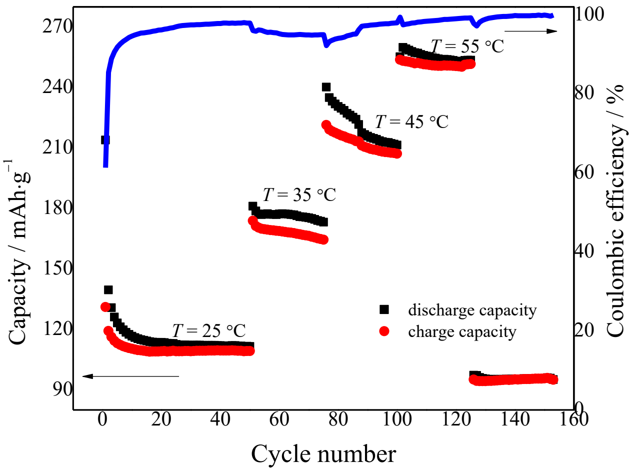

Fig 1. Charge/discharge performance of anatase TiO_2 NTAs in LiTFSI/C_2C_2imTFSI electrolyte at different temperatures at current rate 3 C

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Quinone-bromide redox flow battery with inexpensive negolyte based on anthraquinone sulfonation products

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Redox flow batteries (RFB) is a promising secondary chemical source of current for long-term energy storage used for smart energy networks [1]. Recently the attention of researchers has been attracted to various RFBs organic redox couples which are characterized by good kinetics, availability of primary products and variability: the addition of certain functional groups can significantly change the solubility or standard potential of the redox pair.

Anthraquinone-bromine RFB was presented in [2], where anthraquinone-2,7-disulfonic acid used as negolyte can be synthesized by relatively simple anthraquinone sulfonation process. This RFB demonstrated promising characteristics, however, the possibility to use the products of synthesis as negolyte was not demonstrated ether in this or in subsequent papers.

In this study, a series of anthraquinone sulfonic derivatives was obtained by sulfonation of anthraquinone with oleum varying following key parameters: synthesis time, concentration of reagents, temperature. As a result, we obtained various mixtures of anthraquinone (2,6 and 2,7-) disulfonic acids as well as monosulfonic acids, the quantitative ratios of which were estimated using deconvolution of cyclic voltammetry data.

The resulting mixtures were tested as negolyte in anthraquionone-bromine RFB. It was shown that the characteristics of tested RFBs do not differ and in some cases even surpass the similar characteristics for RFBs, using pure anthraquinone-2,7-disulfonic acid as negolyte. For example, a mixture of products with a total concentration of 0.212 M disulfonic acid with the trace concentration of monosulfonic derivative demonstrated maximum discharge power about 145 mW/cm^2 (similar characteristic for RFB with pure anthraquinone-2,7-disulfonic acid was 105 mW/cm^2), energy efficiency and electrolyte utilization during cycling tests are about 70 and 85%, respectively. The data obtained confirm the possibility to use sulfonation products of anthraquinones as negolytes in organic RFB.

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The Successive Reduction Approach in Water in Oil Microemulsion Synthesis of Bimetallic Nanoparticles

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Ever growing need for energy has led the world to the edge of complete exploitation of fossil fuels, and the verge of irreversible environmental damage. It is imperative that we start fully relying on renewable sources, and for that, the electrochemical energy conversion and storage systems are required. Fuel cells, as energy conversion devices, are the most promising ones, using hydrogen or small organic molecules - SOMs as fuels (energy carriers). SOMs such as methanol, ethanol or formic acid have been used as an alternative to hydrogen, due to their low production cost, safe handling and use in the liquid sate and ease of implementation in the existing distribution systems. The reactions of methanol oxidation (MOR) and formic acid oxidation (FAOR) are studied in the present study.

State of the art anodic catalysts are usually platinum group metals (PGM) or their bimetallic combinations, in the form of nanoparticles (NPs), supported on high area carbons. One of the ways to synthesize them is the water in oil microemulsion method [1], which allows the use of surfactants and capping agents to affect the particle shape. Since MOR and FAOR are structure sensitive, NP shape and composition affect the catalytic performance. In our previous work we have successfully synthesized shaped Pt/C catalysts, and then bimetallic PtAu/C catalysts with this method, using the simultaneous reduction approach (both precursors are in the same microemulsion - ME) [2,3], while at this point the successive approach is employed (reduction of Pt in one ME, joining with other ME with Au precursor, second reduction), with low Au loading of less than 5%. The results of Energy Dispersive X-ray Spectroscopy (EDS) and electrochemical characterization are shown in Fig 1 (A-D). This way, more Au was obtained on the surface, as expected, which contributed to a better catalysis in FAOR – higher activity and favoring of a direct mechanism (due to more pronounced ensemble effect), and better catalyst stability in MOR (due to weaker CO bonding). The change in particle shape and surface structure with extremely fine distribution of Au, and a higher share of Au at particle surface, as benefits of the successive reduction synthesis procedure have a high impact on catalytic performance.

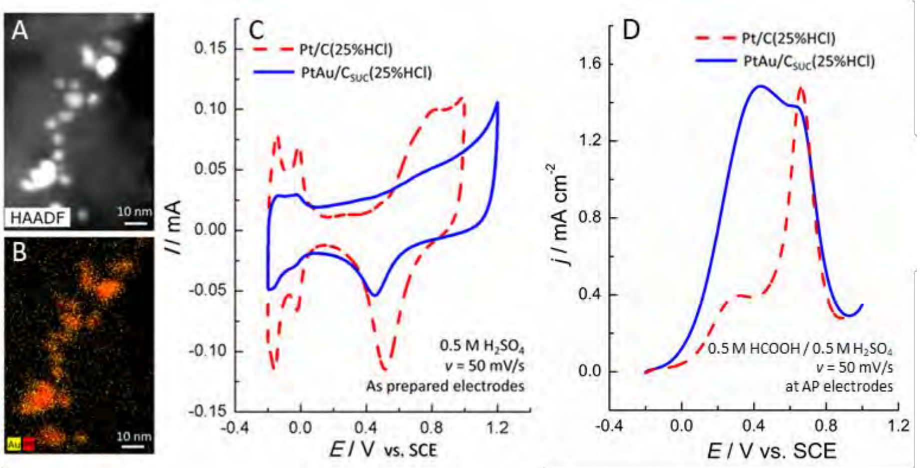

Fig 1. HAADF image (A) and EDS map (B) of the PtAu/C$_{SUC}$(25%HCl) sample; initial CV at AP surface of Pt and PtAu samples (C), initial anodic scan of FAOR at AP surface of Pt and PtAu samples (D)

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Electrolyte pH as a means of controlling the selectivity of CO_2 reduction reaction and the kinetics of H_2 evolution reaction

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It has long been recognized that metal-electrolyte interactions at the electrified solid-liquid interface play an important role in controlling the intrinsic kinetics of electrocatalytic reactions. Additionally, reaction (heterogeneous and/or homogenous) induced concentration gradients in the diffusion layer can further alter the mechanistic pathways of electrocatalytic reactions by modifying the availability of the competing reactant species. In this framework, (local) electrolyte pH is one of the most important parameter in aqueous electrocatalysis, since it affects both the composition and the structure of the electrical double layer. In this work, we emphasize the importance of this crucial parameter, by first discussing the role of electrolyte pH in controlling the selectivity of the CO_2 reduction reaction (CO_2RR) on Au electrodes in weakly buffered bicarbonate electrolytes and thereafter, by presenting a detailed quantitative understanding on the pH dependent kinetics of hydrogen evolution reaction (HER) on Au electrodes under alkaline conditions.

At present, the economic feasibility of electrochemical CO2RR remains an issue, primarily due to efficiency losses from the concomitant HER. In this context, a better understanding of polarization induced local pH gradients at the interface and their role in the kinetic competition of CO2RR and HER will be crucial for the optimization of this reaction. Here, we will present a new implementation of the well-known rotating ring-disk electrode (RRDE) technique to study the role of local pH gradients on the selectivity of CO2RR under well-defined mass transport conditions[1]. In essence, this work shows that enhanced mass transport acts as a pH regulator and suppresses the local build-up of hydroxyl ions, which in-turn inhibits the HER (water mediated) during CO2RR and dictates the overall Faradaic selectivity of these two competing reactions (as shown in Figure 1).

Interestingly, this work also shows that OH^- ions affect the kinetics of water reduction reaction on Au electrodes such that the HER activity improves with the increasing pH. This deviates strongly from the previously reported trend for the Pt(111) surface and the well-established trends for pH dependence of HER under acidic pH conditions[2]. In addition to the pH dependence, we observe that the activity of HER also increases with the cation concentration in the electrolyte. Here, we will show that these two seemingly independent trends are in-fact caused by the same phenomenon, namely, the cation assisted enhancement of the rate determining water dissociation step (Volmer step). It is well known that the interfacial electric field shifts with the electrolyte pH (on the RHE scale). We propose that this pH dependent electric field induces cation concentration changes near the surface, leading to a pseudo pH dependence for HER (as shown in Figure 2). We also present a quantitative analytical model formulated from theory, which captures the pH (and/or mass transport) dependence of HER as an inherent feature of the cation dependence of HER which further validates our experimental findings. Therefore, this work provides crucial insights for the design of optimized electrolyte pH conditions for HER in alkaline media.

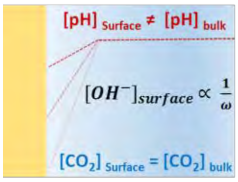

Figure 1

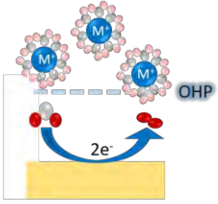

Figure 2

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Interactions of Zn(II) with DNA Holliday Junction Assemblies: Genotoxicity of $ZnCl_2$ and Its Prevention

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Over the past two decades, DNA-based nanotechnology has largely focused on developing ultrasensitive bioelectronic nanodevices that are capable of processing environmentally generated signals.[1] Consequently, branched DNA Holliday Junctions (HJ) have attracted increased attention as cation-controlled nanoscale switches.[2-3]

In this work, we investigated the feasibility of controlling reversible switching of DNA HJ and formation of the DNA HJ-based origami scaffolds by Zn^{2+} ions, introduced in the form of either chloride or sulfate. Besides being one of the most abundant essential microelements in the human body, Zn^{2+} ions are not directly involved in redox reactions in biological systems,[4] which have made them appealing cation candidates for our research. The conformational switching of HJ was monitored using Fluorescence Resonance Energy Transfer (FRET) between donor and acceptor dyes each located at the terminus of one of the arms, while liquid Atomic Force Microscopy (AFM) was used for visualization of the switching process by the construction of DNA origami assemblies in Zn^{2+} solutions.

Surprisingly, the Cl^- ions, unlike the SO_4^{2-} ions, detrimentally affected the HJ switching process in the presence of Zn^{2+} ions. The evidence of that outcome was clearly visible using AFM imaging technique which displayed Zn/Cl-containing deposits formation within DNA HJs, which was also confirmed electrochemically. However, further research demonstrated that the presence of ascorbic acid or other antioxidant species prevented the effect of zinc removal from solutions caused by Cl^- ions. Thus, this work represents a plain way of controlling the switching/assembly processes induced by zinc chloride with the presence of biologically relevant antioxidants and allows a flawless design of new DNA HJ-based nanoswitching biosystems.

Keywords: DNA Holliday Junction, zinc cations, FRET, AFM, nanoswitching

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Ultrasensitive Electrocatalytic Analysis of *Escherichia coli* at DNA modified Gold Electrodes

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Sensitive, specific and rapid detection of bacterial colonies is becoming the need of the hour. Food spoilage, prevention of pathogenic infections and antimicrobial resistance put such detection systems at highest priority in food and medicine industry. [1] Among these microbial communities, the bacterial strain of *Escherichia coli* (*E. coli*) is most commonly found, with pathogenic and non-pathogenic strains being biomarkers of bacterial contamination. [2] Here, we developed a novel electrochemical assay for *E.coli* utilizing DNA as electrical wires, mediating electron transfer between gold electrodes and a well-known DNA intercalator, Methylene Blue (MB).The binding of *E. coli* specific target DNA to the capture DNA-modified gold electrode surface triggers the intercalation of MB present in solution within the hybrid structure. The signal from MB is further electrocatalytically amplified in reaction with a commonly used redox indicator ferricyanide whose electrochemical reduction is otherwise very slow on the DNA-modified surfaces. The developed assay allows down to attomolar detection of both synthetic and isolated *E. coli* DNA and RNA. The high sensitivity of the assay allows direct application of it in point-of-care and industrial platforms for analysis of raw or minimally processed samples.

Keywords: Electrochemical detection, Methylene Blue, Escherichia coli

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A novel CuO/Cu-N-C electrocatalyst-based gas diffusion electrode for the selective electro-reduction of CO_2

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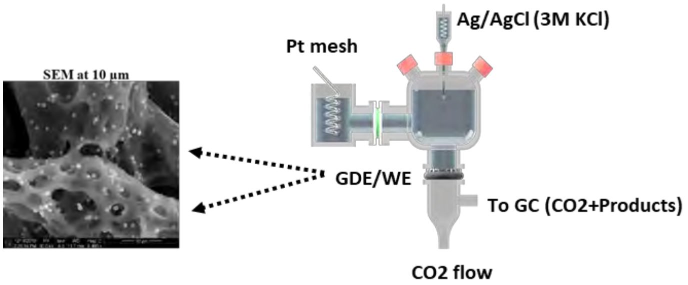
The efficient electrochemical conversion of CO_2 to valuable energy-dense chemicals and synthetic fuels such as e.g. ethylene and ethanol is an attractive route for curbing greenhouse gas emissions.[1] However, the reduction of CO_2 is quite tedious as it involves multi proton-multi electron transfer reactions to overcome the inherent large energy barriers. Among various metals, Cu is the only metal that can reduce CO_2 into various value-added multi-carbon (C_{2+}) products.[2] Recently, metal-nitrogen-doped carbon materials (M-N-Cs) have emerged as a class of materials displaying up to 80% faradaic efficiency for CO formation (Fe-N-C) at comparatively low overpotentials (-0.55 V vs. RHE)[3] compared to metals alone. These M-N-C materials contain $M\text{-}N_x$ sites which have been shown to be active sites in the CO_2RR. Gas diffusion electrodes (GDEs) were recently reported as ideal electrodes for conversion of gaseous reactants in aqueous environment at relevant current densities (> 200 mA cm^{-2}).[4] The presence of a three-phase boundary allows a higher gas concentration to reach the catalyst's active sites, since a high solubility of gaseous reactants in aqueous environment is no longer required. Additionally, the use of GDEs allows that CO_2RR is performed in alkaline environment which was shown to favour the C-C coupling and formation of high C products ($C\geq2$) via CO_2RR together with suppression of the H_2 evolution reaction. Herein, we report the fabrication of a CuO/Cu-N-C type electrocatalyst directly immobilized on the current collector by using a benzoxazine monomer[5] and copper acetate as carbon, nitrogen and Cu precursor, respectively. This involves direct catalyst synthesis on the current collector by spray coating the mixture of the benzoxazine monomer and Cu acetate onto a carbon paper followed by pyrolysis. The catalyst coated carbon paper is further converted into a gas diffusion electrode by spray coating of a Teflon layer. As control experiment, the "classical" approach in which the catalyst is pre-synthesized and then spray coated on a commercial gas diffusion layer is also presented and the results are comparatively discussed. Scanning electron microscopy (SEM) was used to assess the electrode morphology. The influence of the electrode structure on the CO_2RR selectivity performed in H-type modified cell in alkaline environment (pH ~ 13) evaluated based on gas chromatography (GC) and high liquid performance chromatography (HPLC) will be presented.



Scheme: Electrochemical cell and SEM image of CuO/Cu-N-C.

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Electrospinning of carbon nanofibers decorated with Pt nanoparticles as fuel cell electrocatalysts

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Nanoscale architecture is very important for complex and advanced products like electrocatalysts. The position and coordination of each atom define its activity, selectivity and also stability. In order to understand and optimize these properties, it is crucial to have control over these nanostructures. For the optimized operation of electrocatalysts also the mass transport of reactants and products must be optimized. Typically movement of molecules is effected at the nano- to micro-scale. In order to combine both, mass transport and intrinsic electrocatalyst activity, electrospinning is recognized as a suitable method, where nano-sized fibers are produced with great precision and relative ease. [2]

The objective of electrospinning, as a simple, versatile, cost-effective and up-scalable approach, in our study was to fabricate one-dimensional mesostructured carbon nanofibers of controlled hierarchical features with Pt nanoparticles on the surface as electrocatalyst model electrode (Fig. 1a,b,c). By taking advantage of the modern advanced characterization techniques like in-situ heating transmission electron microscopy (TEM) and electrochemistry (cyclic voltammetry, methanol oxidation reaction, oxygen reduction reactions, floating electrode) together with classical characterization like scanning electron microscopy (SEM), we reveal several new insights. By appropriate annealing protocol (Fig. 1d), we were able to produce carbon nanofibers decorated with Pt nanoparticles from polyacrylonitrile (PAN) mixed with Pt salt in one step; with no Pt trapped inside the carbon matrix. This synthesis provides a facile way to produce effective high surface area Pt-electrodes.

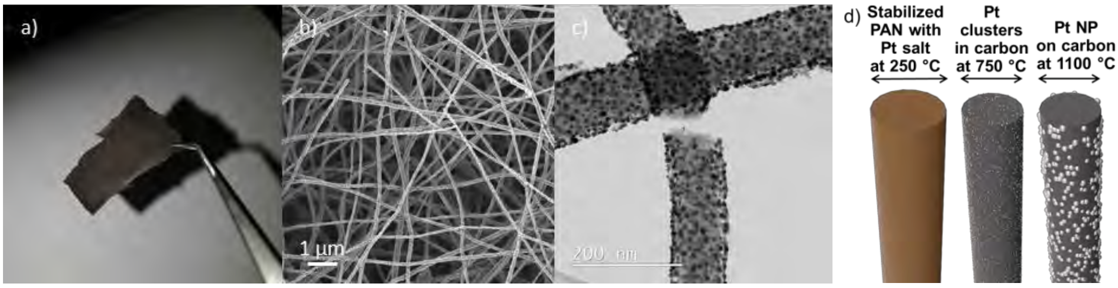

Figure 1. a) photography, b) SEM, c) TEM and d) STEM of electrospun and subsequently annealed at 1100°C Pt/C electrode. In the c) and d) Pt nanoparticles are clearly distinguished on the carbon nanofiber.

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Structure activity investigation of Co_3O_4 nanoparticles for the OER reaction using scanning electrochemical cell microscopy

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Conventional ensemble-based electrochemical techniques such as rotating disk electrode and rotating ring disk electrode experiments provide insight into the electrocatalytic reactions and henceforth provide information about activity, possible reaction mechanisms and understanding about the long-term stability of materials of interest. However, any further improvement in the intrinsic activity for a given electrocatalytic reaction of such nanoparticles necessitates a thorough understanding of their structure-property relationships, particularly with respect to the size and shape-dependent electrocatalytic activity. Importantly, in case of non-precious metal-based catalysts, the impact of the exposed crystal lattice including defects, local compositional changes as well as its dynamics during catalytic turnover needs to be understood to allow for a rational design of improved electro catalysts for complex multi-electron/multi-proton transfer oxidation reactions.[1,2]

In this direction, scanning electrochemical cell microscopy (SECCM) provides vital insight into the structure-activity correlation at the nanoscale and is effective to study the morphology-based activities within the confined area on a single substrate.[3,4] In the present work, Co_3O_4 nanoparticles with different structural morphologies were studied using SECCM for the oxygen evolution reaction. Co_3O_4 nanoparticles with different morphologies were deposited on glassy carbon plates as well as on transmission electron microscopy (TEM) grids. Cyclic voltammograms and linear sweep voltammograms were collected at nanoparticles from a large number of investigated droplet-wetted spots in a suitable potential range in presence of a redox couple as internal potential standard. Electrochemical results of SECCM scan were correlated with the particle morphology imaged by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to elucidate the structure activity relations.

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Environmentally Friendly Synthesis of Platinum Group Metals Nanoparticles and Electrocatalytic Materials Based on Them

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Nanoparticles of platinum group metals (PGMs) in particular Pt, Pd, Rh, are still the most effective catalysts for processes that occur in low-temperature fuel cells [1]. As a rule, chemical and electrochemical methods for producing nanostructures containing nanoparticles of PGMs are based on a "bottom-up" approach, when simple elements (atoms, ions or molecules of precursor compounds) form systems with a complex structure. We propose a "top-down" method for producing electrocatalysts (M/C) based on Pt, Pd and Rh nanoparticles, which is based on the electrochemical dispersion of metal electrodes (Pt, Pd or Rh) under the action of an alternating pulse current.

For the M/C catalysts preparation two metal electrodes (Pt, Pd or Rh) with the same area immersed in the suspension of carbon support Vulcan XC-72 (CabotCorp., 240 m^2g^{-1}) in aqueous electrolyte contained Na^+ cations. The electrodes are connected to ac source operating at 50 Hz, current density 1 A cm^{-2}. Bulk metal electrodes were disperse to nanosized metal particles. Then, suspension was filtrated; prepared catalyst was rinsed with H_2O to a neutral pH and dried at 80°C to constant weight.

The mechanisms of the formation of Pt, Pd, Rh nanoparticles in the conditions of electrochemical dispersion were established [2-4]. It has been established that platinum and rhodium electrodes are dispersed to Pt and Rh nanoparticles, while palladium electrodes are dispersed with the formation of Pd-PdO particles. Electrocatalystic activity of synthesized materials was studied using ethanol and formic acid oxidation reactions as an example and a high catalytic effect compared to standard materials was detected.

Based on the data obtained on the processes of electrochemical dispersion of Pt, Pd and Rh electrodes and the formation of metal nanoparticles under the conditions of electrochemical dispersion of metals, we developed methods for the synthesis of Pt/C, Pd-PdO/C and Rh/C materials and investigated their electrocatalytic activity in anode processes [2-4].

Thus, the proposed method M/C obtaining as a result of electrochemical dispersion of metals is technologically simple and environmentally safe because it does not involve the use of organic solvents and capping agents.

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Understanding the electrified interface of Cu-aqueous solution for CO electroreduction

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The conversion of greenhouse gases such as CO_2 into renewable fuels and chemicals is one of the most important technological and environmental challenges facing humanity. Electrochemical reduction of CO_2 and CO on Cu is a promising and sustainable alternative to produce fuels and chemicals, while contributing to close the unbalanced carbon cycle [1]. Recently, efforts have been dedicated to find rational description of the mechanism of both CO_2 and CO reduction on Cu, which continues being focus of debate [2]. Well-defined studies on Cu single-crystalline surfaces are key to elucidate the properties of the Cu-aqueous electrolyte interface, necessary to understand the electrocatalytic properties of Cu.

Herein, we study the interfacial properties of Cu(100) and Cu(111) in contact with different classical electrolytes such as phosphate buffer solutions, bicarbonate solutions and 0.1M NaOH solutions. In this study, we have combined cyclic voltammetry and the laser induced jump temperature technique to elucidate the structure of the Cu-electrolyte interface. Voltammetric experiments aim to provide the fingerprint of both Cu(111) and Cu(100), to be used as a parameter control of the surface state and experimental conditions in studies with Cu [3][4]. The laser induced temperature jump technique has been employed to obtain information about the distribution of the charge on both Cu(111) and Cu(100) surfaces, and then determinate their potential of zero charge (*pzc*) [5]. Overall, we discuss different aspects that we consider essential while investigating the interfacial properties for both CO and CO_2 reduction on Cu: evolution of the voltammogram features at different selected potential windows, specific anion adsorption and pH effects. This experimental study provides deep insights of the interfacial properties of Cu(111) and Cu(100) which are crucial to reach deeper understanding of the reduction of CO_2 and CO on Cu electrocatalysts.

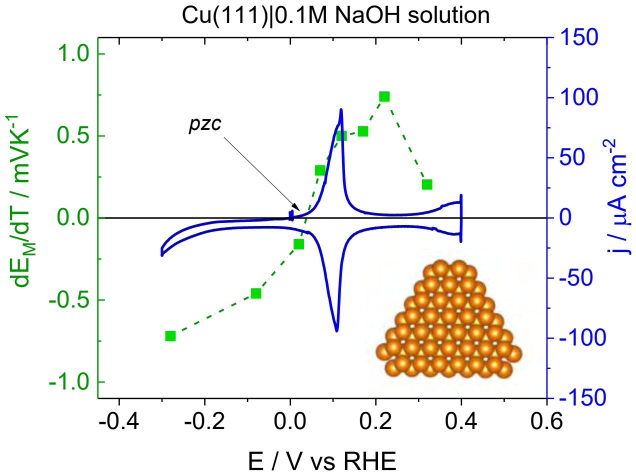

Figure 1: Blank voltammogram of Cu(111)-0.1 M NaOH solution interface at 50mV/s and thermal coefficients of the interfacial potential drop.

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Hardness and Wear Resistance of Multilayered Ni-P Films Fabricated by Pulsed Electroplating

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Industrial chrome plating, which has excellent hardness, corrosion resistance and wear resistance, has been widely used for various industrial products. In the plating process, hexavalent chromium specified as a substance of very high concern by environmental regulations is used. Therefore, plating technologies replacing the conventional chromium plating, such as trivalent chromium plating and Ni-based composite plating, have been studied. In particular, multilayer plating in which different kinds of metal layers are alternately laminated, has been also studied as one of the methods to improve hardness and wear resistance of the plated film. We focused on a multilayered Ni-P film to create a plated film that have hardness, wear resistance and corrosion resistance. In this study, multilayered Ni-P films were fabricated by pulsed electroplating, and the effect of multilayering on hardness and wear resistance was evaluated.

A stainless steel SUS303 (thickness 3 mm) was used for the substrate. Typical pretreatments such as mirror polishing, degreasing, acid treatment, and Ni strike plating (0.1 μm thick) were performed. In a multilayered Ni-P plating process, a Ni plating bath containing additives such as phosphonic acid, sulfur-containing organic compounds and others was used. A pulsed constant current was applied to the substrate in the plating bath to fabricate multilayered Ni-P films with different layer thicknesses and layers structures. Heat treatment was performed at a predetermined temperature to harden the films. The plated films obtained by the above process was used as specimens (multilayered films). For a reference, a monolayer Ni-P film was prepared by applying a constant current (monolayer film). Each specimen had a total plating film thickness of 10 μm. The cross section of each specimen was observed by SEM and STEM. Trace components in the film were analyzed by SIMS (Secondary Ion Mass Spectrometry) and 3D atom probe tomography. The Vickers hardness of each specimen was measured under a load of 25 gf. Wear resistance was evaluated using a reciprocating sliding tester in the air, at room temperature, under non-lubricated or lubricated conditions. The worn scar was observed to measure the worn volume quantitatively.

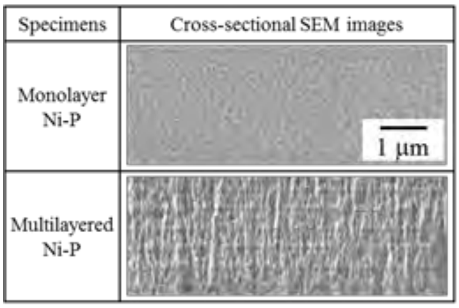

Fig. 1. Cross-sectional SEM images of a monolayer and a multilayered Ni-P films

The cross-sectional microstructures of the monolayer and the multilayered (layer thickness: 500 nm) Ni-P films after annealing are shown (Fig. 1). The monolayer film showed a smooth surface, while the multilayered film showed a layered structure. Analysis of the trace components in the multilayered film showed that P concentration hardly changed and the concentration of the elements such as sulfur and so on derived from the additives increased along the boundary of each layer. This is presumably because the additives were adsorbed on the plated film surface during the period when no current was applied and then were incorporated into the film during the subsequent period when a current was applied, in the pulsed electroplating process. The multilayered structure was maintained even after heat treatment, which is probably due to the suppression of grain growth by the additives solid-soluted between the layers.

Hardness and wear resistance of each film were measured. There was no significant difference in hardness between the monolayer and the multilayered films. The multilayered film exhibited about 1.3 times higher wear resistance than the monolayer film under non-lubricated. This result was discussed by fractography and molecular dynamics simulation for the Ni-P films. During the sliding test, cracks seem to occur not only on the surface of the film but also the inside due to the effect of shear stress distribution. Multiple cracks probably propagated and combined to cause significant delamination in the monolayer film. On the other hand, the interfaces between layers seem to suppress crack propagation in the multilayered film, resulting in small delamination, though cracks occur as in case of the monolayer film.

The above results suggest that multilayering is effective for improving wear resistance, maintaining hardness in the multilayered Ni-P films.

Solid state ionic conductors based on Lu-doped δ-Bi_2O_3

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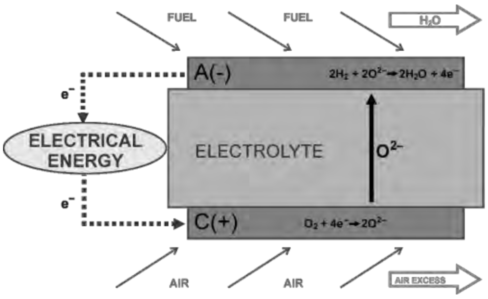

Regarding limited fossil energy resources and hence the increasing demands for new highly efficient and environmentally friendly energy conversion devices, the widespread use of solid oxide fuel cells (SOFCs) might become a keystone in near future. An SOFC is consisted of dense electrolyte which is sandwiched between two porous electrodes. Since the electrolyte is the most important part of an SOFC, oxide ion conductors applicable in SOFCs became the hot topic of modern research. The main requirement is to find a stable dense electrolyte material with increased conductivity at intermediate temperature. Two commercial electrolytes, yttria stabilized zirconia (YSZ) and gadolinia doped ceria (GDC), are far to be ideal. The use of YSZ requires operating temperatures above 1000 °C while devices based on GDC are not efficient enough due to GDC lower conductivity at intermediate temperatures.

The best candidate for an electrolyte in intermediate temperature SOFCs is undoubtedly fluorite structured bismuth oxide, i.e. δ-Bi_2O_3, being the fastest known ionic conductor. However, this material is unstable upon heating/cooling but the use of dopant, such as Tm, led to the impressive stability and high conductivity at intermediate temperatures [1]. Our findings indicated that Lu-doped δ-Bi_2O_3 could show even better performances since Lu is smaller and more rigid dopant than Tm.

In this study, the possibility to stabilize δ-Bi_2O_3 in Bi_2O_3–Lu_2O_3 system was investigated. Two starting mixtures of α-Bi_2O_3 and Lu_2O_3 with the following compositions $(Bi_{1-x}Lu_x)_2O_3$, $x = 0.20$ and 0.25, were dry homogenized in an agate mortar, heat treated at 750 °C for 3 h and then slowly cooled. The obtain powders were characterized by XRD and DTA techniques. Based on these results, the targeted cubic single-phase δ-Bi_2O_3 was successfully obtained within both systems. The unit cell parameter of obtained Lu-doped δ-Bi_2O_3 decreases as the dopant content increases, as expected since Lu^{3+} is smaller cation than Bi^{3+}. According to cyclic DTA curves, no phase transitions (25 – 980 °C) were observed for both phases, $(Bi_{0.8}Lu_{0.2})_2O_3$ and $(Bi_{0.75}Lu_{0.25})_2O_3$, indicating that these δ-Bi_2O_3 phases are stable.

Afterwards, half of obtained quantity of each powder was mechanochemically treated (in planetary ball mill Retsch PM-100) in order to decrease the crystallite size. Namely, before performing EIS measurements the powders undergo to pressing and then sintering to obtain dense ceramic pellets. This is also important for their future application in SOFC since the density of almost 100% is mandatory in order to avoid the direct contact of air (oxygen) and fuel (hydrogen). The density of sintered pellets obtained from both untreated and mechanochemically treated powders will be compared. Using EIS technique, the ionic conductivity will be measured for the samples having the highest density. We expect that these materials will exhibit the conductivities which are higher than those obtained for Tm-doped δ-Bi_2O_3 (0.1 – 0.4 S cm^{-1} at 550 – 800 °C).

Such stability and extraordinary conductivity would open the possibility for application of $(Bi_{0.8}Lu_{0.2})_2O_3$ and $(Bi_{0.75}Lu_{0.25})_2O_3$, which could result in the significant enhancement of electrochemical performance of intermediate temperature SOFCs but also in their good stability over long time service.

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Fe_2O_3-HC and Fe_2N-HC Composites as Negative Materials for Sodium-ion battery

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Sodium-ion batteries (SIBs) are a low cost and high performance alternative to lithium-ion batteries. [1] Hard carbon (HC) has graphitic regions but overall a disordered structure. HC exhibits fairly good performance as a SIB negative electrode material with over 250 mA h g^{-1} of reversible capacity. The majority of its capacity is utilised near 0V (*vs.* Na^+/Na). [2] Metal oxides and nitrides (MO and MN) have high theorical capacities due to a conversion mechanism in which they are reduced to the metal. [3] Our interest is combining MO or MN with HC to increase the capacity oh HC whilst mitigating some of the deficiencies in the oxide or nitride, including cost and volume changes, by supporting them in nanoparticle form on HC surfaces. [4] Here we have used a hydrothermal method to coat iron (II) oxalate on HC surfaces and calcined the precursor in air to obtain Fe_2O_3-HC composites. Heating the same precursor in ammonia results in Fe_2N-HC composites. The composites were tested in sodium half-cells. The hydrothermal process reduced the performance of the HC itself, but the conversion materials added significant extra capacity to that of the HC and this extra capacity persisted during cycling. Future work will aim to find routes to such composites that do not damage the performance of the HC host but do allow the extra capacity to be accessed.

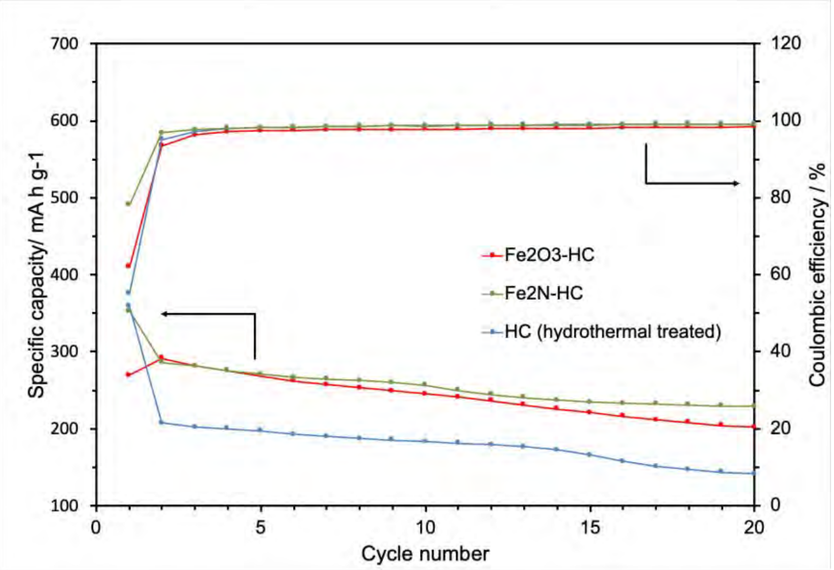

Fig 1 cycling performance of HC (after hydrothermal treatment), Fe_2O_3-HC and Fe_2N-HC between 2 and 0.001V (*vs.* Na^+/Na) at 100 mA g^{-1} in sodium half-cells.

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Novel Double Passivation Galvanic Displacement Method for Production of High Performance Pt-alloy Electrocatalysts

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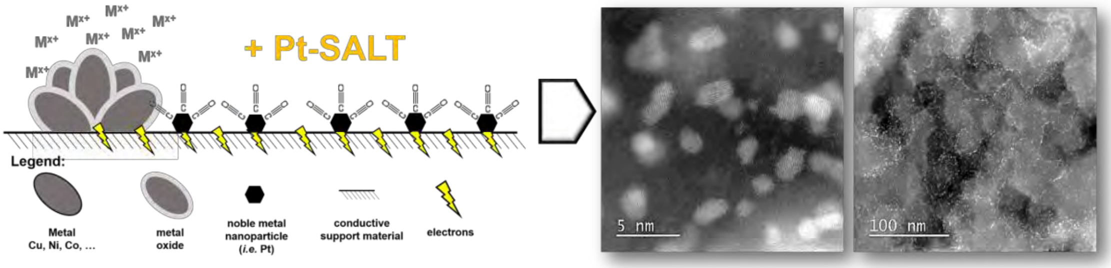
The most vital part of proton exchange membrane fuel cells (PEMFC) – the electrocatalyst still contains too high quantities of critical raw material platinum (Pt). While so-called non-PGM catalysts are expected to become the solution in a quite distant future, the current state-of-the-art approach of lowering the need for Pt can be achieved by alloying Pt with other transition metals. While Pt-alloys (Pt-M; M = Cu, Ni, Co, ...) are already pretty well understood and have already by-far exceeded the targeted goals for sluggish oxygen reduction reaction (ORR), methods for its facile and high scale production are still rather limited. We hereby present a novel approach towards well-known galvanic displacement (GD) method that was initially made popular by R.R. Adržić with the Pt-monolayer electrocatalysts.[1]

Our "trick" is a unique "double passivation" approach towards galvanic displacement method.[2,3] The method enables facile (energy efficient), highly reproducible on several grams scale, water-based (green) production of carbon supported Pt-M nanoparticles. The method offers great flexibility over the electrocatalyst design such as (i) the choice of the sacrificial metal (M), (ii) variation of the chemical composition of alloy (Pt:M ratio), (iii) variation of total metal loading (Pt+M) on carbon support or (iv) even variation of the carbon support itself. Among other benefits of the double passivation method, the sacrificial M on carbon (M/C) precursor does not need to have M in the form of nanoparticles, as well as the methods exploits only spontaneous processes that occur at room temperature and ambient pressures. We have tested the method reproducibly on gram scale or above with respect to 4 different commercially available carbons, 4 different Pt:M chemical compositions, 4 different total metal loadings (Pt+M) and 3 different sacrificial M (Cu, Ni and Co which are the most promising state-of-the-art Pt-alloys).



Scheme 1: Novel double passivation with galvanic displacement method.

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Single Bacterium Detection By Cellulase-Linked Sandwich Immunoassays

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Rapid detection of microorganisms in water, food and air is the 1st step in protection of human health. According to WHO, pathogenic bacteria, being one of the major human health threats, caused 15 million deaths only in 2010 and 13 million deaths are estimated for 2050. Sensitive, specific, and yet inexpensive electrochemical biosensing approaches can provide the required tools for fast and robust analysis of pathogens and thus disease prevention [1-3].

Here, I discuss our recent achievements in the development of electrochemical "label-free" sensing approaches for detection of bacteria based on hydrolase-linked DNA and immunoassays on magnetic beads (MB). While bacterial DNA/RNA can be detected at a 1 fM level [4], electrochemical aptamer-based and immunoassays on MBs allow single bacterium cell detection (**Figure 1**), at a cost below 1-2 € that favorably compete with the existing standard microbial counting and quantitative PCR analytical schemes. Fundamental problems and benefits of a single cells detection as compared to traditional 1:1 affinity DNA and protein assays [4,5] and arising specificity issues are discussed.

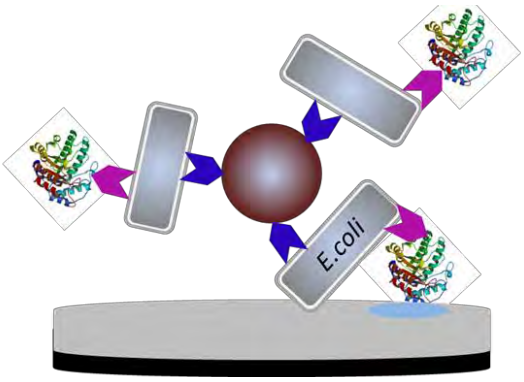

Figure 1: Schematic presentation of the cellulase-linked sandwich assay on MBs. An *E. coli* cell is sandwiched on MB between the aptamer and antibody; the sandwich is labelled with cellulase that digests the nitrocellulose film on the electrode surface. Such digestion changes electrical properties of the film-modified electrodes, which is electrochemically detected.

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Investigation on Layered Double Hydroxides as Anode for Lithium-Ion Batteries

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NiAl layered double hydroxide (NiAl LDH) with nitrates in its interlayer has been studied as anode material for lithium-ion batteries (LIBs). The electrochemical study demonstrates that the NiAl LDH materials can be applied as anodes with a very high specific capacity, with an initial discharge capacity of 2222.0 mAh g^{-1}. The excellent Li^{+}-storage performance is attributed to the expanded interlayer space of the NiAl LDH pillared by the interlayer nitrates, providing effective paths for Li^{+} diffusion [1-4]. CV curves show evident oxidation and reduction peaks corresponding to the flats of charge and discharge in the galvanostatic profile. In this work, we highlight the importance of the binder on the cycling stability. Na^{+} alginate can improve the stability respect to electrodes prepared with PVDF. The hypotesis is that Na^{+} alginate as binder can estabilsh strong bonding between pillared sites which leads to a lower exfoliation of the material during cycling and consequently improve the stability performances.

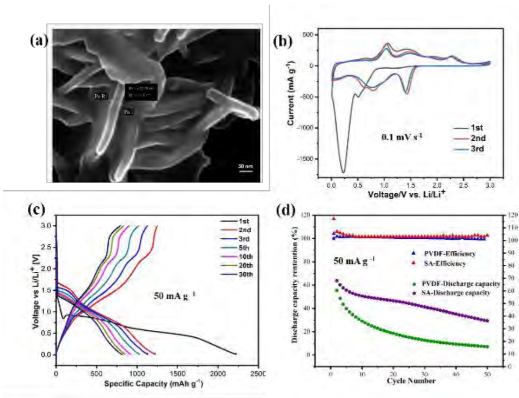

Fig. NiAl LDH's: (a) FE-SEM, (b) Cyclic voltammetry (CV) curve with PVDF as binder, (c) Charge-discharge profile with PVDF as binder (d)cycling performance with PVDF and Na^{+} alginate as binder.

Acknowledgments:

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Mechanistic analysis of the catalytic oxidation of epinephrine by an immobilized multicopper oxidase from *Thermothelomyces thermophila* with the FTacV technique

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Several chemical scenarios, concerning the reaction of redox enzymes with their substrates, can be accessed electrochemically with the most common electrochemical technique for the kinetic analysis of enzyme reactions being cyclic voltammetry. When direct electron transfer between the enzyme and the electrode surface is possible, some problems that occur are the low currents and the dominance of capacitance currents. One attractive alternative to overcome such problems is the use of FTacV (Fourier transform alternating current voltammetry) which has the advantages of both enhancing the Faradaic signal and eliminating the capacitance [1,2]. In this work, a kinetic analysis is made concerning the reaction of an electroactive immobilized enzyme with a free substrate, based on a Michaelis-Menten scheme, the proposed kinetic equations are investigated numerically, under different reaction states (transient or steady state for the reaction intermediate as well as quasi or complete reversibility of the electrochemical step) and the dependence of two chief observables is examined. The FTacV method is applied experimentally for an immobilized laccase-like multicopper oxidase from *Thermothelomyces thermophila*, *Tt*LMCO1 [3], and its reaction with epinephrine is monitored. From the experimental findings it is shown that the intristic characteristics of the system do not lead to the extraction of the desired kinetic data, although indications on the relation between the kinetic constants is revealed. Finally, the response of the third harmonic for the first additions of epinephrine at subnanomolarity range can be exploited for the detection of epinephrine at rather low concentrations.

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3-cyano propionic acid methyl ester as alternative solvent for high voltage dual carbon lithium ion capacitors

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Lithium ion capacitors (LICs) are aimed to cover the gap between lithium ion batteries (LIBs) and electrical double layer capacitors (EDLCs), providing both high energy and high power densities. However, the performance of LICs can be hindered due to the high reduction potential of some negative electrodes or the limited electrochemical stability of the electrolyte at high potential values, ultimately reducing the operational voltage window of the device. Thereby, in order to increase the operational voltage window of LICs and target high energy applications, the use of new solvents providing a wide electrochemical stability window at high potentials is foreseen.

In this work we report for the first time the use of 3-cyano propionic acid methyl ester (CPAME), with vinylene carbonate (VC) as additive, as an alternative solvent when targeting high voltage LICs [1]. In view of the promising viscosity, conductivity and electrochemical stability window, its use in a LIC is explored. To this end, a hard carbon (HC) is selected as the negative electrode, while an activated carbon (AC) is the preferred choice as the positive electrode, both being biomass (olive-pits) waste derived. Electrochemical characterization of the HC shows good specific capacities at both low and high current densities (*e.g.* 322 mAh g^{-1} at C/10 and 80 mAh g^{-1} at 10 C). In addition, the cyclic voltammogram of the AC reveals a stable electrochemical potential window rising to 4.6 V *vs.* Li^{+}/Li. This fact allows to develop a LIC operating at 1.5 - 4.5 V able to deliver high energy and high power density values (*i.e.* 121 Wh kg$^{-1}_{AM}$ at 299 W kg$^{-1}_{AM}$ and 69 Wh kg$^{-1}_{AM}$ at 2217 W kg$^{-1}_{AM}$, Figure 1). Moreover, it shows a capacitance retention of 70% after 5000 cycles.

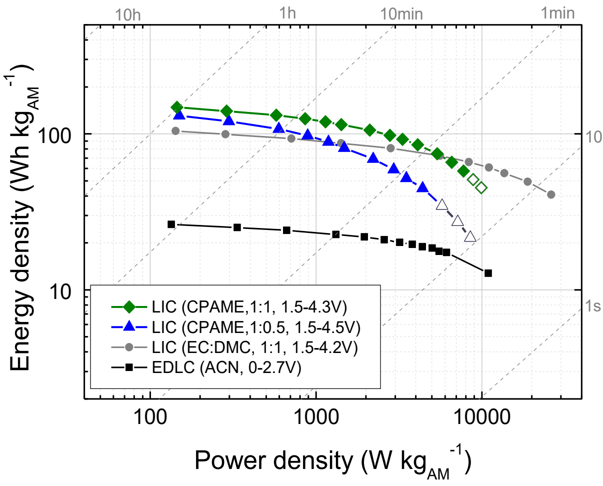

Figure 1. Ragone plot with the studied LICs and their EDLC counterpart. Open points show where lithium plating occurs.

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Intermetallic Compounds as Platform Materials to Discriminate Electronic and Geometric Effects in Electrocatalysis

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Bimetallic systems can provide enhanced electrocatalytic activity and/or selectivity due to their altered electronic and/or crystal structure, which changes the adsorption energies of the reactants and/or the products in a chemical reaction [1-3]. These two effects are the main parameters governing the catalytic properties of a material. However, they are often interrelated and can be difficult to distinguish from one another due to segregation and random distribution of the elements in substitutional alloys. Intermetallic compounds are formed by at least two elements and possess an at least partially ordered crystal structure different from that of the constituting elements. In combination with the reduced segregation tendency, they provide an excellent material platform for a knowledge-based approach aiming for the evaluation and optimization of structural and/or electronic effects in heterogeneous catalysis (Fig. 1). The gradual substitution of one element by another from a different group in isostructural intermetallic compounds allows a systematic variation of the total number of electrons per unit cell with a minor variation of the cell parameters [4]. Thus, electronic influences can be evaluated with only small structural influences. In addition, the substitution of one element by another from the same group allows a systematic variation of the cell parameters, thus interatomic distances, with the same total number of valence electrons per unit cell, therefore limiting electronic influences.

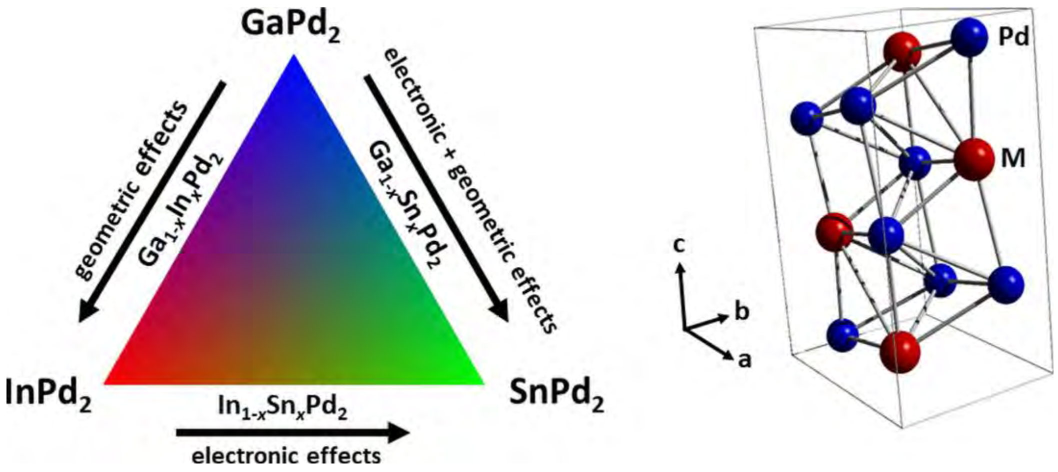

Figure 1. The isostructural triangle MPd_2 *(*M *= Sn, In or Ga) with the corresponding unit cell.*

Herein, the correlation between electronic, geometric and electrocatalytic properties in the electrochemical methanol oxidation are investigated by increasing the valence electron count per unit cell by substitution of indium (three valence electrons) with tin (four valence electrons) in the isostructural series $In_{1-x}Sn_xPd_2$. Furthermore, geometric effects were evaluated by decreasing the volume of the unit cell by substitution of indium with gallium in the isostructural series $Ga_{1-x}In_xPd_2$. The use of unsupported bulk electrode materials enables the evaluation of the electrochemical behaviour of the material without support interference or other phenomena that might occur with the use of supported materials. The results contribute to the knowledge-based development of catalytic materials for electrochemical energy conversion by direct experimental evidence of electronic influences using isostructural intermetallic compounds as platform materials and model catalysts.

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The use of nucleotides for the sustainable manufacture of high-performing graphene cathodes for NaO_2 batteries

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Graphene has emerged as a promising material due to its superior electrical conductivity and highly accessible 2D area. The real integration of graphene as electrode material in energy storage devices, however, requires the development of sustainable and scalable approaches for its production and processing. Adenosine monophosphate (AMP) has proven its suitability to act as an intercalation agent for the obtention of high-quality graphene nanosheets by electrochemical exfoliation of graphite. In addition, this natural biomolecule can act as a dispersing agent, enabling the production of stable graphene aqueous bio-inks that can be readily processed into 3D graphene aerogels.[1] This graphene aerogel obtained by an easy, sustainable and scalable method has shown a superior performance in a Na-O_2 battery cathode using a glyme-based electrolyte. The Na-O_2 battery assembled with this unprecedented cathode delivered a discharge capacity as high as 9.64 mAh cm^{-2} (**Figure 1**) while performed 95 cycles with a 97 % efficiency at shallow cycling (0.5 mAh cm^{-2}) and high current density (0.2 mA cm^{-2}). The origin of such performance was studied and ascribed to the phosphate groups present in the natural biomolecule, which is adsorbed on the surface of the graphene sheets comprising the porous aerogel cathode **(Figure 1).** The phosphate groups modify the nucleation mechanism of the discharge products by i) enhancing the interaction of the cathode with oxygen reactive species and ii) catalyzing the ORR/OER reactions which take place while discharging/charging metal-air batteries. The latter aspect is of paramount importance for the real implementation of rechargeable Na-O_2 batteries as their reversible cycling is the major bottleneck for their commercialization.[2]

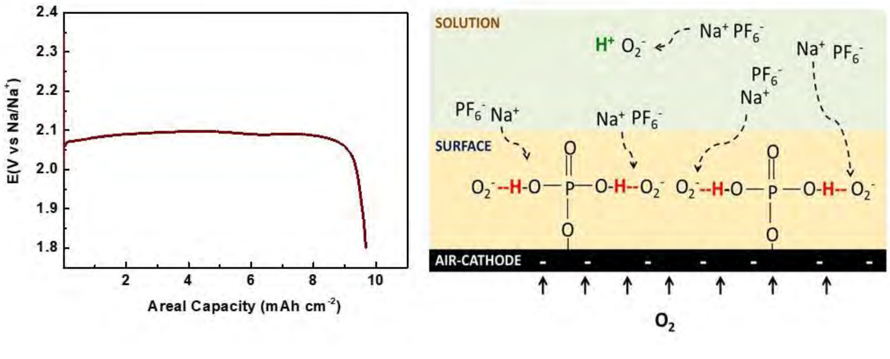

Figure 1. Discharge of the AMP-derived graphene aerogel at 0.2 mAh cm^{-2} using a glyme-based electrolyte and proposed effect of phosphate groups on the cathode performance.

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The effect of trap states in semiconductor electrodes on their optoelectronic and photoelectrochemical behavior

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Detailed mechanistic understanding of the optoelectronic features is a key factor in designing efficient semiconductor (photo)electrodes. In situ spectroelectrochemical methods and electrochemical impedance spectroscopy provides an opportunity to scrutinize the effect of trap states on the optical and electronic properties of semiconductors. Different metal oxides and halides were studied, and results gathered for TiO_2, NiO and CuI will be presented in this talk. The absorption bands in the UV-visible spectrum and the Raman spectral features were directly influenced by the applied bias potential. These spectral changes correlate with the alterations observed in the electrical conductivity. Interestingly, the population/depopulation of the trap states, that are responsible for both the changes in the optical and electronic properties, occur in a different potential/energy regime.

In the function of these results, we can optimize the properties of the given semiconductor to make it the most appropriate for different applications. The hole transporting behavior of p-type semiconductors is very important for solar cell research, however if there are a lot of defects inside the band gap which can trap the holes, we must know the conditions, which allow us to use the transporting layers efficiently. In the case of TiO_2, hydrogen treatment causes a remarkable increase in the donor density by creating oxygen vacancies which behave as shallow electron donors. I will show how the presence of these states affects the (photo)catalytic activity and the photoelectrochemical performances of TiO_2.

Deep dive into thin film copper oxide layers

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Copper has been extensively explored especially since the revolution of the telecommunication industry. Exposed metal copper to air, moisture or temperature forms an oxide duplex film consisting of cuprous (Cu_2O) and cupric (CuO) oxides. Understanding the composition of the oxide layer is immense for the corrosion and conductive properties of copper. The oxide film of well-defined quality can passivate the underlying metal copper thus protecting from environmental damage.

Various surface analytical techniques have been implemented to characterize and differentiate both surface oxides. A double sweep cyclic voltammetry (DSCV), as a promising technique for the quantitative characterization of copper oxide films has been successfully applied to study oxide films at μm scale (1, 2). Reduction of Cu_2O and CuO in the selected electrolytes shows a clear separation between two cathodic well-assigned peaks.

However, as the oxide film gets thinner, characterization of the nature of copper oxides is challenging. This is due to the fact that the stability range of Cu_2O covers only a small potential window and therefore the electrochemical separation of both oxides strongly depends on the thickness of the whole film as well as on its architecture.

In the present paper, we will demonstrate how the DSCV method must be adapted in order to identify the composition of thin oxide films on nm scale. Both the reduction kinetics and the potential separation require a compromise between the oxide differentiation and the quantitative thickness determination. Hence, even in thin oxide layers of 10 nm we were able to distinguish the ratio of both oxides with a sensitivity of 1nm. This opens the opportunity to record external physical parameters such as influence of humidity and type of underlying copper substrates, which can significantly influence the oxide growth and its behavior at high temperatures.

The crystallographic orientation of modified copper substrates will be discussed in relation to its ratio of copper oxides. An impedance study combined with X-ray photoelectron spectroscopy (XPS) as well as Fourier-transform infrared spectroscopy (FTIR) reveals the structure within the copper oxide layers.

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Electrochemical study of the effect of composition on the CO_2 reduction reaction at $Pd_{100-x}Cu_x$ nanoalloys

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Carbon dioxide (CO_2) is a greenhouse gas that produces global warming with undesirable climate effects, such as sea level rising and erratic weather patterns. Reducing the CO_2 atmospheric concentration is a current research priority. Among the different technologies proposed to achieve this goal, the electrochemical reduction reaction of CO_2 (CO_2RR) to useful low-carbon fuels (CO, CH_4, CH_3OH, HCOOH, …) is particularly attractive given its compatibility with renewable electricity sources. Metal catalysts in various forms have been tested for CO_2RR, including bulk or nanostructured metals, and more recently, bimetallics, for which the catalytic activity, efficiency and selectivity is boosted [1].

In this work, we report on the synthesis and characterization of bimetallic $Pd_{100-x}Cu_x$ nanoparticles with different compositions and its application as nanoelectrocatalysts for CO_2RR. Few studies using this kind of alloy under different configurations (Cu overlayers on Pd [2], Pd-decorated Cu electrodes [3], mesoporous CuPd films [4], CuPd NPs of different mixing patterns and morphologies [5]) have pointed out the higher performance of bimetallic PdCu with respect to each single metals (higher current density, lower overpotentials, higher resistance to CO poisoning). In most of these works, electrochemistry has been used as a tool for product generation (i.e. quantitative electrolysis at selected potentials) without attention paid to recording and interpreting the electrochemical signals. More in-depth electrochemical studies could improve our understanding of CO_2RR at $Pd_{100-x}Cu_x$ compounds.

Here, we present and in-depth electrochemical study of CO_2RR at $Pd_{100-x}Cu_x$, with a special focus on the influence of the bimetallic composition on the CO_2RR response and the related CO-poisoning. Cyclic voltammetry and chronoamperometry have been selected, in combination with a cavity microelectrode (CME) for the first time. The low-distorted voltammetric signals obtained with the CME have evidenced that for alloys with low or moderate Cu content (up to 50 at.%) the typical CO_2RR inhibition peak, related to CO blocking Pd active sites, becomes a current plateau. This indicates not only a better tolerance of $Pd_{100-x}Cu_x$ towards CO poisoning but also the attainment of a pseudo-steady state where mass transport should be controlled by diffusion. The synergy between Cu and Pd is thus established for the first time at the level of the voltammograms.

We have observed that the chronoamperometric responses exhibit three well defined regions corresponding to 1) double layer charging and diffusion/reaction establishment, 2) beginning of CO poisoning by formation of a CO adlayer and (3) final collapse of the catalytic activity at a critical time, t_c, which depends directly on the bimetallic composition. A plot of t_c vs. Pd content exhibits a clear volcano shape, from which ~ $Pd_{70}Cu_{30}$ is identified as a close to optimal composition in terms of CO tolerance and $Pd_{35}Cu_{65}$ as the composition from which the advantage of alloying Pd with Cu is lost. Based on these studies, the potential benefit of developing a pulse-based method to increase the lifetime of Pd-based catalysts is demonstrated.

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Performance optimization of an integrated battery and electrolyser system

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The absence of large-scale electricity storage methods is currently one of the major factors limiting widespread deployment of renewable energy sources such as wind and solar power [1] [2]. The Battolyser –an integrated nickel-iron battery and alkaline electrolyser– can bridge the gap between intermittent energy production and consumption fluctuations [3]. During charging, the pocket electrodes consisting of $Ni(OH)_2$ and $Fe(OH)_2$ powder form NiOOH and Fe, which can evolve oxygen and hydrogen. Thereby, the charged electrodes can electrocatalytically split water efficiently to produce hydrogen as a long-term storage fuel, while fast discharging of the electrodes can provide electricity for short-term fluctuations in renewable energy availability.

To upscale the Battolyser device, a comprehensive characterization of the design parameters was necessary. Using these parameters, we have developed and validated a COMSOL multi-physics model describing the integrated operation of the Battolyser. The model was validated using experimental results, and new configurations of design parameters have been compared and optimized for the upscaling of this lab-scale prototype. Here, we present an optimization study of the integrated electrolyser and battery system with regards to the energy efficiency. The model will be used to design larger and optimized device configurations to allow for efficient large-scale energy storage.

To further optimize the performance of the integrated device, a study on the synergistic effects of alkali metal cations in the electrolyte was performed. In alkaline electrolysis different cations have different effects on the overpotentials of oxygen evolution [4] while certain alkali metal cations are used to improve the cycleability of nickel iron batteries. The addition of LiOH in the KOH electrolyte used in Ni-Fe batteries is widely reported [5]. However, this is not usual in alkaline electrolysis. The integration of both devices must therefore be taken into account when choosing the electrolyte for the Battolyser. Here, we present the effect of the electrolyser alkali cations on the battolyser charge/discharge cycles and electrolyser functionality. This study presents the electrocatalytic response to a change in electrolyte composition. Overall the results presented will allow for ideal electrolyte selection in the upscaling of this device, providing efficient and integrated short-term and long-term energy storage requirements.

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Prussian Blue – Nickel Hexacyanoferrate as Superstable Electrocatalyst for Bioanalysis and Biotechnology

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Prussian Blue (PB) is known to be the most advantageous (thousands times more active and selective than platinum) electrocatalyst for hydrogen peroxide reduction, the very reaction catalyzed by the enzyme peroxidase. PB possesses unique properties of the electrocatalyst allowing elaboration of sensors and biosensors with advantageous analytical characteristics [1]. Probably the only disadvantage of the PB is its inherent instability, particularly in neutral solutions. Non-iron transition metal hexacyanoferrates (isostructural to PB, but chemically and mechanically more stable than PB), especially nickel hexacyanoferrate (NiHCF), being silent in the electrocatalysis of H_2O_2 reduction serve as excellent matrixes for stabilization of Prussian Blue.

In this work PB based advanced hydrogen peroxide transducer is deposited onto screen-printed electrode structures (Rusens Ltd, Russia) and stabilized with NiHCF, both in open circuit mode. In severe conditions under 1 mM H_2O_2 the developed electrodes retain the response for more than one hour. Moreover, we could confirm that operational stability of the oxidase-based biosensors can be significantly improved stabilizing the transducer used. The method describing stabilization procedure was done according to [2]. To develop the biosensors suspending the suspension of lactate / glucose oxidase aqueous solution in isopropanol containing γ-aminopropyltriethoxysilane / Nafion analogue was deposited onto the top of iron-nickel hexacyanoferrate modified electrode. The dynamic range of PB-NiHCF based biosensors is similar to range observed for conventional PB based ones but their performance characteristics are dramatically improved.

Immuno- and DNA- (RNA-) sensors as well as affinity based analytical kits comprise an important part of vital activity for modern society since they are used in a variety of areas from medicine to agriculture. For signal generation these devices use labels, among which one of the leading positions belongs to the enzyme peroxidase. Novel rapidly growing field of modern science is synthesis of nanozymes – nanoparticles with enzyme-like activity. The most progressive and actual application of nanozymes is to substitute natural enzymes in various fields of science and technology allowing to avoid the most important problems of the enzymes: their inherent instability and relatively high cost. Nanozymes obviously require advanced catalysts.

Techniques of catalytic synthesis of PB nanoparticles and elaboration on it basis the nanozymes "artificial peroxidase" were just published [3]. Catalytic rate constants of the nanozymes are up to 4 orders of magnitude higher as compared to the natural peroxidase. Except for the activity defeating even the natural enzyme, the advantages of the reported PB nanoparticles over the known peroxidase-like nanozymes are enzymatic specificity (an absence of oxidase-like activity) and an ability to operate in physiological solutions, similarly to the enzymes.

Unfortunately, PB nanoparticles demonstrate inherent instability in neutral and basic solutions (pH>6). In current research stabilized by nickel hexacyanoferrate composite core-shell PB nanoparticles were synthesized. We also deposited obtained nanoparticles onto screen-printed electrode structures to produce hydrogen peroxide sensors and biosensors. Composite PB-NiHCF nanoparticles demonstrate around one order of magnitude improved stability compared to PB nanoparticles (pH 7.4).

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Microwave-assisted fabrication of $V_3O_7 \cdot H_2O$ nanowires/reduced graphene oxide composite for aqueous zinc-ion battery application

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Rechargeable multivalent ion batteries have attracted significant technical and scientific interests, especially aqueous zinc ion batteries, due to their low cost and high safety.[1] Layered $V_3O_7 \cdot H_2O$ is a promising material due to easy intercalation of doubly charged Zn^{2+} ions. This is due to the special structure with extended hydrogen bonding between VO_6 octahedrons and VO^5 trigonal bipyramids.[2] In addition, the mixed oxidation state of vanadium (IV and V) can help improving the electric conductivity. With the addition of reduced graphene oxide, rGO, the active materials obtain high electrochemical stability. Herein, we have synthesized $V_3O_7 \cdot H_2O$ nanowires/reduced graphene oxide composite by a microwave method through controlling pH by a nonoxidizing acid and have thoroughly investigated the reaction mechanisms of the synthesis. A composite used as cathode of the zinc-ion battery can deliver a high specific capacity of 385.7 mAh g^{-1} at a current density of 4 A g^{-1}. Impressively, the capacity retention after 1000 cycle is up to 96%. This excellent performance suggests that vanadium oxide and rGO composite may be a good cathode candidate for aqueous zinc ion battery.

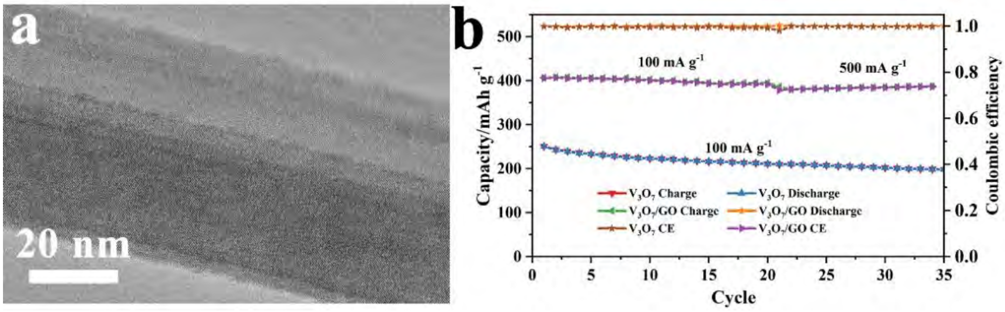

Figure 1 TEM image of the $V_3O_7 \cdot H_2O$ nanowire (a) and cycling performance of the pure $V_3O_7 \cdot H_2O$ nanowire and $V_3O_7 \cdot H_2O$ nanowires/reduced graphene oxide composite (b).

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Restructured Bismuth Metal-Organic Framework Boosts Mass Activity for Carbon Dioxide-to-Formate Production

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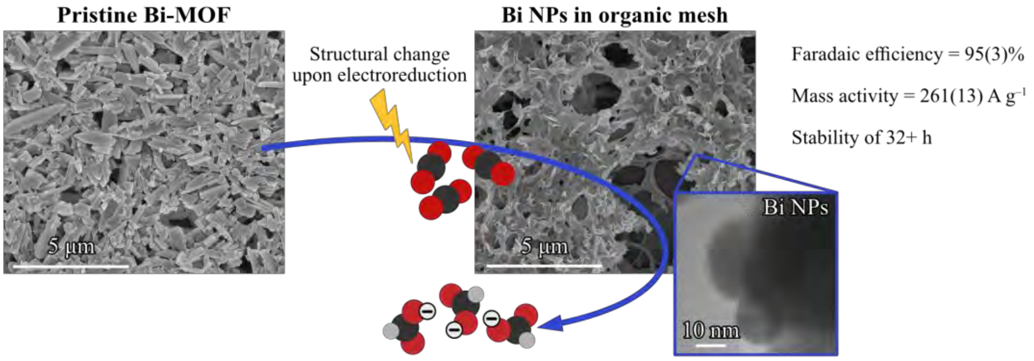
Limiting anthropogenic carbon dioxide (CO_2) emissions and exploiting such compound as a resource to produce valuable chemicals, fuels and materials, especially when using renewable energy inputs, are key strategies to reduce our carbon footprint.[1] We proved in this work that the metal-organic framework (MOF) Bi(1,3,5-tris(4-carboxyphenyl)benzoate), or Bi(btb), promotes the efficient and selective electrocatalytic CO_2 reduction reaction (eCO_2RR) to formate, a relevant compound in industrial applications and in fuel cell technology.[2] The MOF Bi(btb) acts as a pre-catalyst and under eCO_2RR conditions undergoes a structural reconstruction that generates an organic porous matrix embedded with highly active Bi nanoparticles. In a typical H-cell configuration, this new material produces formate with Faradaic efficiencies up to 95(3)% at 770 mV overpotential and exhibits a metal-based mass activity which is competitive or even larger than most state-of-the-art catalysts reported in scientific literature.[3-6] The electrocatalytic features of the MOF-derived material and the structural change leading to the active Bi nanoparticles were thoroughly monitored with a broad ensemble of techniques.[7]



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In-Depth Stability Studies of Gold Nanoparticles – Electrochemistry Coupled with TEM and ICP-MS Investigations

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Gold nanoparticles (NP) have attracted significant attention in electrocatalysis, especially for CO_2 reduction to CO [1] and production of H_2O_2 through $2e^-$ oxygen reduction [2]. Despite numerous works on the activity, only a few studies have dealt with the equally important descriptor for the applicability of Au catalysts – stability under the relevant electrochemical conditions [3,4].

Here we present an in-depth study of the electrochemical stability of commercial carbon-supported Au nanoparticles (Au/C). Stability of Au/C samples was probed by an adapted accelerated stress test: 10 000 fast scans (1 V/s) in the potential region between 0.3 V and 1.13 V (*vs.* Ag/AgCl) in a 0.05 M H_2SO_4 electrolyte with and without the presence of chlorides. A significant loss of Au was observed even in Cl^- -free electrolyte, while the addition of Cl^- promoted Au dissolution, as expected (Fig. 1a). TEM imaging clearly showed a variety of changes upon degradation, such as loss and growth of the Au NPs and appearance of various shapes of NPs (Fig. 1b-e), which were more expressed in the presence of chlorides. This implies that different degradation mechanisms occurred simultaneously, including dissolution, redeposition, Ostwald ripening, agglomeration, particle detachment and carbon corrosion. Coupling an electrochemical flow cell with ICP-MS confirmed that the dissolution of Au is highly affected by the presence of chlorides and transient in nature under the applied conditions [5].

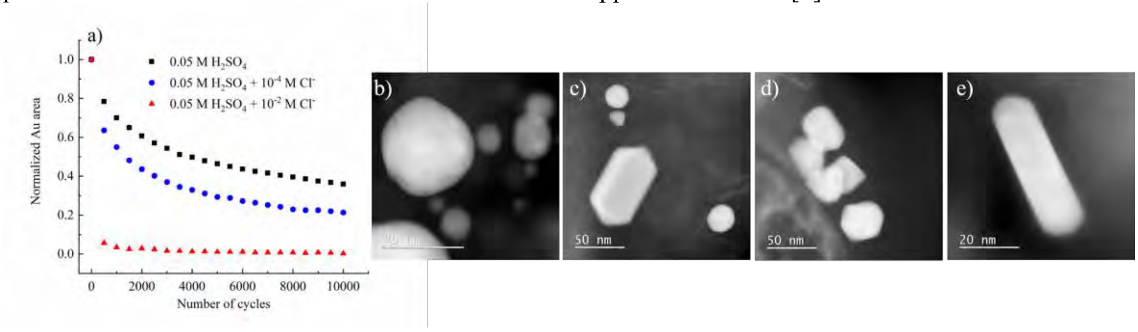

Figure 1. (a) Gradual loss of electrochemical surface area of Au during cycling; (b) STEM imaging of fresh Au/C sample and of samples degraded in: (c) 0.05 M H_2SO_4; (d) 0.05 M H_2SO_4 + 10^{-4} M Cl^- and (e) 0.05 M H_2SO_4 + 10^{-2} M Cl^-.

Besides assessing the stability of Au/C NPs, the results obtained in this study are opening a new perspective towards another very important subject – electrochemical recycling of Au from end-of-life electrodes and, more importantly, from non-conductive samples containing not only Au, but other precious metals as well (such as electronic waste). As shown by Hodnik *et al.* for Pt [6], transient dissolution can be mimicked by alternate changes between oxidative and reductive potentials on metal by alternate exposure to oxidative and reductive gasses. A parallel study on the application of this approach for recycling of gold is currently underway in our laboratory.

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A self-powered glucose sensor with optical readout

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As main energy source, glucose has a critical role for living organisms. Diabetes, a metabolic disorder, which is linked to elevated blood glucose levels in the body, can have vast impacts for the people affected. Hence, the glucose levels must be closely monitored, making easy-to-apply point-of-care devices, which allow on-site monitoring of the glucose level in the blood, highly desired. Therefore, substantial efforts have been put into the creation of miniaturized low-cost point-of-care devices[1], which can be handled by the patients themselves.

In this context, we report the fabrication of a self-powered glucose sensor with an optical readout system for simple and fast optical readout with the bare eye. The sensing device consists of a glucose-powered biofuel cell compartment and a poly(3,4-ethylenedioxythiophene) (PEDOT)-based electrochromic reporter for optical readout, both immobilized on a single screen-printed electrode chip (Figure 1). A glucose/O_2 biofuel cell is used, in which glucose is oxidized to glucono-δ-lactone by the oxygen-insensitive enzyme PQQ-GDH that is wired to the electrode surface by the low potential redox polymer poly(1-vinylimidazole-*co*-allylamine)-[Os(dmxy-bpy)$_2$Cl]Cl.[2] A bilirubin oxidase-based biocathode is used for the O_2 reduction to H_2O. The electrochemically deposited PEDOT films reveal a blue color and decolorize upon oxidation by the glucose-limited current of the connected biofuel cell. Using the power output generated by the biofuel cell to oxidize the PEDOT film any necessity for external powering devices is excluded. Thus, the complexity of the system is reduced, showing potential for applications as point-of-care device.

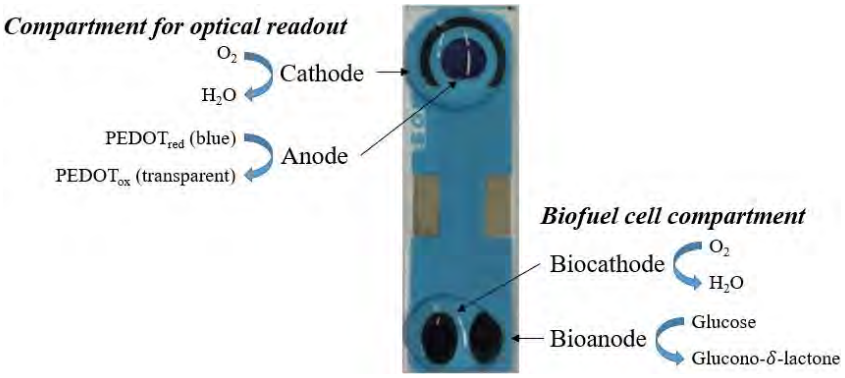

Figure 1: Screen-printed device for glucose detection, consisting of an integrated biofuel cell coupled to an electrochromic reporter for optical readout.

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Cobalt Quaterpyridine Complex Supported on Different Carbon Materials for Selective CO_2 Electrochemical Reduction to CO

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The electrochemical reduction reaction of carbon dioxide (CO2RR) is a promising method for obtaining various carbon-based products such as carbon monoxide CO used in industry. This reaction requires the use of an appropriate electrode material. Molecular materials based on transition metals turn out to be promising catalysts for the CO_2 reduction reaction due to their high selectivity and low overpotentials [1]. The Cobalt 2,2':6',2'':6'',2'''-quaterpyridine complex $[Co(qpy)]^{2+}$ supported on multi-walled carbon nanotubes was shown to be a good candidate with high selectivity and Faradaic efficiency (ca. 100%) for the conversion of CO_2 to CO [2]. It also shows high current densities of up to 19.9 $mA.cm^{-2}$ for an overpotential of 440 mV [2].

Here we show that supporting the $[Co(qpy)]^{2+}$ complex on different carbonaceous materials (carbon Vulcan, graphene oxide GO, reduced graphene oxide rGO, N and N, S doped rGO) induces a significant change in the catalytic current. The nature of the interaction between the support and the complex as well as the onset potential for CO_2 reduction were investigated with cyclic voltammetry, as shown in Fig. 1A. Linear sweep voltammetry coupled to *in situ* FTIR spectroscopy (Fig. 1B) were performed to identify the reaction products and to determine the geometry of the complex on the support. Preparative scale electrolysis was performed on each material to determine the maximum current density and the selectivity for carbon monoxide formation.

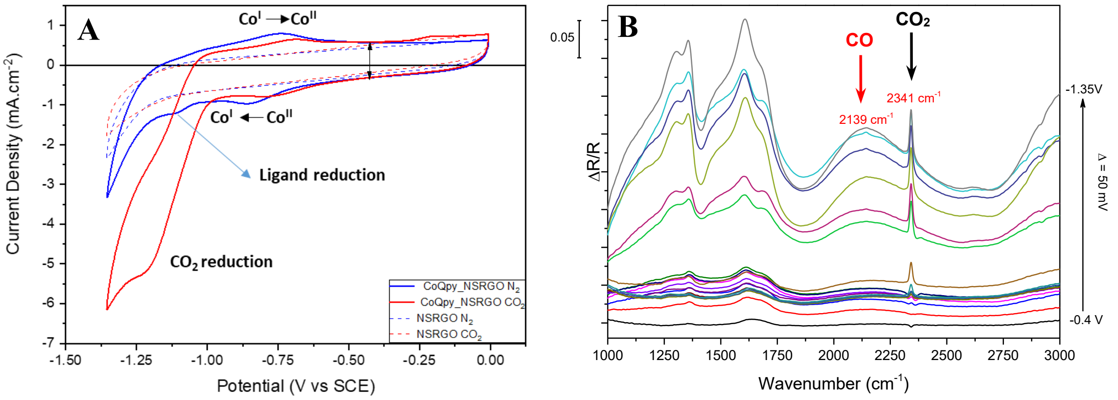

Fig. 1: *Cyclic Voltammograms of Coqpy-NSRGO deposited onto a glassy carbon electrode in 0.5 M $NaHCO_3$ solution saturated in N_2 (blue) and CO_2 (red) at a scan rate v = 50 mV/s **(A)**. Infrared spectra of Coqpy-NSRGO deposited onto a glassy carbon electrode **(B)**.*

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Impact of Mn valence on the current during cyclic voltammetry in manganese oxide and mixed cobalt-manganese oxide

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Among the wide range of transition metal oxides used for the oxygen evolution reaction (OER), manganese oxides have received much attention because their low toxicity and high abundance[1]. Currently, this attention is being shifted to mixed Mn-based oxides, particularly mixed Co/Mn oxides are interesting due to their low overpotential and high stability at alkaline pH[2]. The catalytic properties of Mn-based oxides have been studied in more detail as compared to Co/Mn oxides, as well as in the context of activation and degradation of the material. Degradation is usually associated with changes on surface or bulk composition, long range order or microstructure. These modifications can be electrochemically observed as changes in overpotential at fixed current or vice versa.

We electrodeposited non-crystalline MnO_x and $(Co,Mn)O_x$ films in alkaline electrolyte and their catalytic stability was studied by electrochemical experiments. Changes in the catalytic properties are especially observed in MnO_x such as a decrease in the maximum OER current during 100 cycles and a decrease in the Tafel slope, in contrast with $(Co,Mn)O_x$ where both the OER current and Tafel slope remains fairly constant after 100 cycles. The current profile as function of cycles was studied during 100 cycles at three selected potentials, namely no OER, onset of OER and OER. An additional 10 cycles were performed after a break at OCP for 30 min (Figure 1). For MnO_x, a monotonous decay is observed at all shown potentials, and after the OCP break, the current is only partially recovered. In contrast with $(Co,Mn)O_x$, where the highest potential shows an increase with cycling, which might be related to an activation process. All these results suggest possible structural changes especially in MnO_x films, but since these materials are non-crystalline, X-ray absorption spectroscopy (XAS) was used to study their chemical structure.

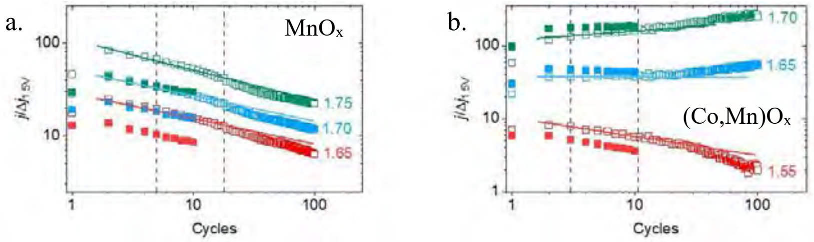

Figure 1. Current profile ($j/\Delta j_{1.5V}$) as function of cycle at selected potentials (shown in figure) for a) MnO_x and b) $(Co,Mn)O_x$. Open square represent data before OCP and solid square after OCP.

The Fourier transform of the EXAFS gives information about the local chemical structure, Co and Mn K-edge spectra suggest an amorphous layered oxide structure. Additionally, the Mn-K edge of $(Co,Mn)O_x$ is shifted to higher energy in comparison with MnO_x, meaning a higher average oxidation state of Mn. The Mn-L_3 edge showed two components in MnO_x: Mn_3O_4 and MnO_2, but after 100 cycles a clear decrease of the peaks corresponding to Mn_3O_4 is observed.

These results suggest that the inclusion of Co in the electrodeposition promotes a higher oxidation state of Mn (between Mn^{3+} and Mn^{4+}) in the structure of the Mn/Co oxides[4], which seems to have key role enhancing stability during catalysis, by means of constant current and Tafel slope. This result agrees with previous reports suggesting more stability in those materials with oxidation states Mn $\geq$+3.7[3]. This study provides insight into the importance of Mn valence for the design of Mn/Co oxide catalysts.

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Elucidating the interaction between Ir and Ti in active and stable iridium/titanium-based OER catalysts by advanced x-ray analytics

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Polymer exchange membrane (PEM) water electrolyzers predominantly employ expensive and rare iridium based anode materials[1], and thus reduction of the noble metal loading will foster their large scale development and deployment. Iridium oxide-based anodes exhibit the best combination of reactivity and stability compared to other anode candidate materials, still they slowly undergo degradation under oxygen evolution reaction (OER) conditions[2]. Considering the high cost of Ir, even a slow dissolution rate presents a challenge for large-scale implementation. The combination of highly active iridium oxide (IrO_x) with a significantly more stable transition metal oxide, e.g. TiO_2, can be a good strategy for stability improvement and reduction of the precious metal loading[3,4]. Considering the semiconducting nature of the Ti oxides and their poor catalytic properties, the chemical and electronic interactions with Ir are thus crucial to result in a long-term stable anode material with high activity. However, the exact nature of the Ir-Ti interaction has not yet been unveiled[5].

To investigate the underlying interactions within the Ir-Ti mixed oxides, co-sputtered libraries of Ir and Ti with a continuous Ir loading gradient of 20 – 70 at.% were annealed at mid-range temperatures to form the mixed oxide. By means of x-ray spectroscopic techniques, insights into the chemical and electronic structure of the resulting material were gained. For instance, depth resolved information of the annealed Ir-Ti alloy libraries was determined using soft and hard x-ray photoelectron spectroscopy in combination with more bulk sensitive photon in/photon-out soft x-ray absorption and emission spectroscopy. Combining the electrochemical activity results with the spectroscopic data, we gain further understanding of the interaction between highly active IrO_x and stable TiO_2, and how this contributes to a better OER electrocatalyst, e.g. preliminary results show that materials containing more than 60 at.% Ir showed catalytic activity comparable to pure IrO_2 while showing a superior stability.

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Investigation and Comparison of Different Recovery Procedures of Polymer Electrolyte Membrane Fuel Cells

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One of the main barriers hindering the commercialization of PEMFC applications is the limited durability caused by a series of chemical and physical degradation phenomena. Mitigation and elimination of the degradation effects has been a research focus during the last several decades. However, some of performance loss can be recovered by certain operation procedures and are therefore considered as reversible losses (also denominated falsely reversible degradation)[1]. Hence, detailed understanding of reversible effects and procedures are of particular interest.

This work evaluates the effectiveness of three recovery procedures. Two are proposed by activities of EU, and DOE and the third is the overnight rest procedure which was recognized as an effective approach in literature[2,3,4]. These three procedures are compared in single cell durability tests using fuel cell dynamic load cycling (FC-DLC). With the polarization curves before and after each recovery procedure the recovered voltage losses (see Figure 1) have been determined. The overnight rest procedure and the EU protocol recovered partial performance, which was not recovered by DOE procedure at low and intermediate current density. However, at current density >1.7 Acm^{-2} all three procedures lead to a recovery of ~60%. Moreover, the recovery efficiency strongly depends on operation history of the cell which was analyzed in this study in detail. Electrochemical Impedance Spectroscopy (EIS) tested before and after each recovery procedure provides insight into the ohmic, charge transfer and mass transport effects during due to recovery (see Figure 2). These preliminary data demonstrate that ohmic resistance is recovered most efficiently by the DOE procedure at low and overnight rest procedure at high current density. Charge transfer resistance is recovered less efficiently by DOE protocol than by the two others. The efficiency of recovery of mass transport resistance is similar for all three protocols.

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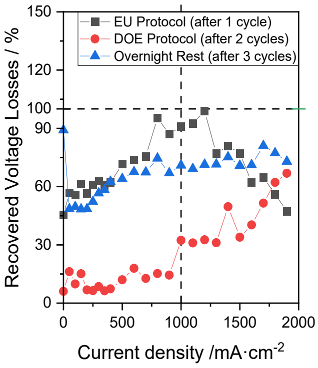

Figure1 Recovered voltage loss of each procedure under different current density

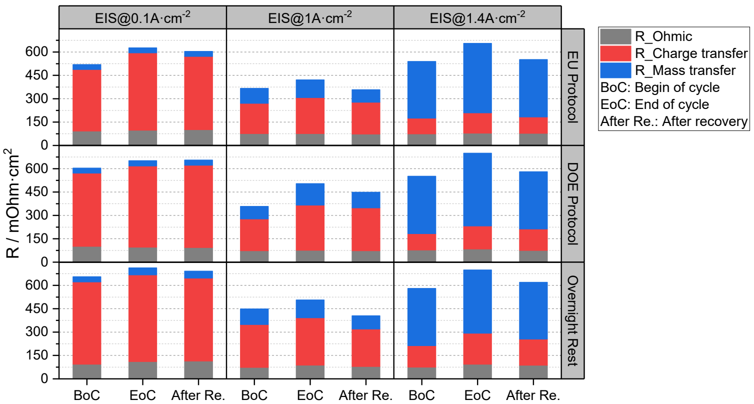

Figure2 Resistance before and after each recovery procedure

Direct CO_2 Reduction on Bimetallic Electrocatalysts

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The main problem with renewable energy sources is their intermittent nature, which leads to a mismatch in power supply and global demand. Here, large scale energy storage of renewable energy by electrochemically converting CO_2 into renewable fuels can solve this dynamicity in the power supply can be smoothed out. However, the electrochemical conversion of CO_2 particularly suffers from low selectivities, due to its complex and multi-step reaction network. In order to selectively produce one specific reaction product, different adsorption sites need to exist on the surface, each of which optimally bind the reaction intermediates of the desired product to the surface. Until now, mainly copper-based electrodes have been shown to be able to convert CO_2 into higher hydrocarbons yet still at high overpotentials and low selectivity [1, 2].

This is where the alloying of different metals in the electrodes comes into the picture. By mixing different metals, a larger range of different adsorption sites can be achieved on the electrode surface. Here, the electrode surface can be more freely tuned by changing its (bulk) composition or by placing one metal upon another host-metal, i.e. near-surface alloying [3]. Hereby, the adsorption properties of the topmost layer are changed by the subsurface atomic layers. One recent example of this is a gold-palladium electrode by Kortlever et al. which showed the production of higher hydrocarbons, which was even able to produce larger hydrocarbons than copper [4]. This is one of the only electrodes that showed the electrochemical production of higher hydrocarbons from CO_2 reduction other than copper. Also, Nickel-Gallium electrodes have shown similar results [5]. These electrodes show the great potential of electrode alloying.

However, not all PdAu electrodes that were tested in literature, observe the formation of hydrocarbons while reducing CO_2 [6, 7]. In our research, we study what our experimental choices (choice of buffer, surface morphology) might be of influence on this observed difference between the different studies.

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EQCM Analysis of Zn Negative Electrode during Deposition/Stripping Processes

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The development of Zn-air batteries with a high energy density of 1350 Wh kg^{-1} is one of breakthrough required to achieve a low carbon society. There are, however, two main challenges concerning the morphology control of Zn deposit and the development of catalyst with high activity for oxygen evolution reaction. Focusing on the negative electrode side, Zn undergoes remarkable shape change during charge−discharge, causing poor cycle performance. At a low current density, electrochemical deposition of Zn results in mossy structure. This is caused by continuous two-dimensional nucleation followed by the formation of protrusions on wide terrace and the suppression of microstep growth toward lateral direction. At a high current density in diffusion-limited condition, dendritic growth is dominant. Strategies for the suppression of non-uniform Zn deposition are mainly classified into following five methods; (1) the use of additives such as metal-ion and surfactant, (2) the change from aqueous electrolyte to/mixing with an organic electrolyte or an ionic-liquid electrolyte, (3) the optimization of substrate, (4) the introduction of anion-exchange ionomer between Zn electrode and electrolyte, and (5) the construction of matrix accommodating shape change. Considering simplification of the processes, the strategy of use of additive is industrially preferred, and we have achieved smooth morphologies of Zn deposit in 0.25 M ZnO/4 M KOH. In our previous reports, it was found that cationic surfactant, trimethyloctadecylammonium chloride (STAC) suppressed the shape change and resulted in smooth and dense morphology. Zeta potential measurements, kinetic current densities observed from Tafel plots, and constant potential electrolysis indicate that quaternary ammonium cations (STAC) with bulky size adsorb to protrusions which are cause of shape change and suppress Zn deposition in the region to promote lateral growth. Although the adsorption of STAC increased an average overvoltage for Zn-deposition/stripping in a symmetric Zn|Zn cell under current density of 10 mA cm^{-2}, significantly stable behavior continued during 200 h. In this work, an electrochemical quartz crystal microbalance was applied to study Zn-deposition/stripping behavior in the aqueous-based electrolyte.

An aqueous-based electrolyte solution (so called alkaline zincate bath) was prepared by dissolving ZnO powder at a concentration of 0.25 mol dm^{-3} (M) in 4 M KOH aqueous solution (13.5 mL). An AT-cut quartz crystal coated with Cu (fundamental frequency; 9.0 MHz) was incorporated into an EQCM cell with a Hg/HgO reference electrode was assembled. The mass change on QCM electrode during Zn-deposition/stripping reactions at a galvanostatic condition was calculated from the change in resonance frequency using the Sauerbrey equation. In addition, we studied the influence of current densities on reversibility based on mass changes.

Graphite as a Positive Electrode Material for Aqueous Zn-based Rechargeable Batteries

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The development of Zn-air batteries with a high energy density of 1350 Wh kg^{-1} is one of breakthrough required to achieve a low carbon society. There are, however, two main challenges concerning the morphology control of Zn deposit and the development of catalyst with high activity for oxygen evolution reaction. Focusing on the negative electrode side, Zn undergoes remarkable shape change during charge−discharge, causing poor cycle performance. At a low current density, electrochemical deposition of Zn results in mossy structure. This is caused by continuous two-dimensional nucleation followed by the formation of protrusions on wide terrace and the suppression of microstep growth toward lateral direction. At a high current density in diffusion-limited condition, dendritic growth is dominant. Strategies for the suppression of non-uniform Zn deposition are mainly classified into following five methods; (1) the use of additives such as metal-ion and surfactant, (2) the change from aqueous electrolyte to/mixing with an organic electrolyte or an ionic-liquid electrolyte, (3) the optimization of substrate, (4) the introduction of anion-exchange ionomer between Zn electrode and electrolyte, and (5) the construction of matrix accommodating shape change. In this study, we focused on concentrated electrolytes. In addition to this, the concentrated electrolytes were applied to anion-intercalation/deintercalation into/from graphite interlayers. Although the reversible capacity based on the intercalation/deintercalation of anions would be much smaller than a capacity obtained from oxygen as a positive electrode material, the reversibility of the reaction thought to be high and stable in a long-life cycle.

Zn-deposition/striping behavior was investigated by galvanostatic charge−discharge tests using an electrochemical measurement system (HJ-1001 SM8A, Hokuto Denko Co., Ltd.) and by cyclic voltammetry (CV) measurements though the use of an electrochemical analyzer (SP-200; Bio-Logic Science Instruments) at a sweep rate of 1 mV s^{-1} at room temperature. In the test of anion-intercalation, graphite powder and PVDF binder were used for the preparation of a slurry electrode. For investigation of the effect of powder size on charge−discharge capacities was also studied.

Figure 1 shows cyclic voltammograms corresponding to Zn-deposition/stripping on a Ti foil as a current collector in aqueous-based electrolytes at a sweep rate of 1 mV s^{-1}. In a dilute electrolyte of $ZnCl_2{\cdot}50H_2O$ (molar ratio), no response originating from Zn-deposition/stripping reactions was observed. This is because of the narrow electrochemical window. Below 0 V, the hydrogen evolution reaction preferentially took place instead of Zn deposition. In contrast, at concentrations of 2.33 or more, reversible deposition/striping reactions were confirmed. When using the concentrated electrolytes, the anion intercalation into graphite interlayer progressed to form partially graphite intercalation compound even in an aqueous-based electrolyte.

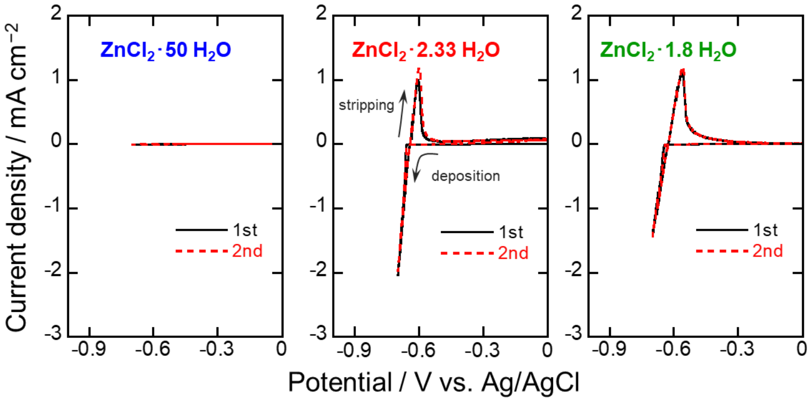

Figure 1 Cyclic voltammograms corresponding to Zn-deposition/stripping on a Ti foil as a current collector in aqueous-based electrolytes at a sweep rate of 1 mV s^{-1}. The counter electrode is Zn foil.

Hydrogen production by electrolysis of methyl pivalate: A first approach to an efficient treatment of PMMA waste

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In recent years, hydrogen has become a focus of research and an essential industrial target area, not only because of its use as an energy carrier and practical employment in fuel cells but also for its role as a significant raw material of the chemical industry [1]. Today, the steam reforming of fossil fuels (primarily methane) is the most common and cost-effective H_2 production process [2]. Notwithstanding its advantages, it requires additional units to separate H_2 from the coproduced CO and CO_2, and it actively contributes to greenhouse gas emissions [3],[4]. Hydrogen can also be produced by electrolysis of water; this environmentally friendly process has taken force lately because it can be easily integrated to the electrical grid and use renewable energy sources (i.e. solar or wind) to produce pure H_2 from water, producing only O_2 as a by-product [5].

However, the energy requirement correlated to the thermodynamic data shows a relative standard cell voltage of around 1.23 V to achieve the water electrolysis reaction at room temperature [6]. Consequently, different researchers have proposed to electrolyze organic molecules instead of water to reduce energy demand. Plastic wastes contain an abundant source of hydrogen and can be a promising renewable feedstock for electrolysis. Among the different plastics, poly(methyl methacrylate) (PMMA) is a widely used polymer in several applications [40]. Even if different recycling methods are implemented, such as thermal and chemical processes, any other processes than the incineration for direct *Energy Recovery* is used. In this sense, the present study proposes a new route to valorize plastic wastes by producing H_2 using an electrochemical process. Due to the complexity and the heterogeneity of real PMMA-based plastics, we decided, as a first approach, to investigate a Methyl pivalate (MP) as a model molecule representative of the polymer containing similar chemical units, including atoms, bonds and functional groups (ester). We studied the electrooxidation of MP in a Polymer Electrolyte Membrane-based (PEM) reactor with an acid membrane (Nafion®) and commercial Pt/C electrodes between 50 and 80°C. This system allows operating in aqueous media without an electrolyte and under continuous conditions. A complete study of the operation conditions was carried out to enhance the production of H_2.

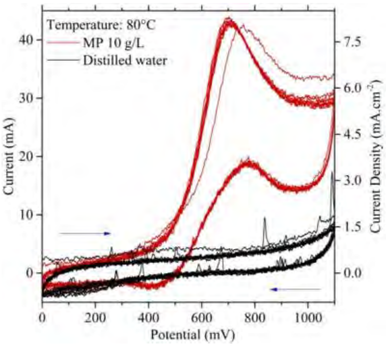

Figure 1. Cyclic voltammetry of water and MP at 80ºC and 10mV/s.

The electrooxidation process of MP shows an entirely different behaviour than the electrolysis of water at similar conditions and higher activity at potentials lower than 1.23 V. Experiences at different temperatures demonstrate that 80ºC is optimal for the electrolysis of MP. As showed in Figure 1, a critical oxidation step takes place at ~700-750 mV when cyclic voltammetry is performed with a second peak registered when the potential is decreasing. That phenomenon is attributed to an unfinished cleavage process of the MP molecule in the surface of the Pt/C anode. Typically, at the presented conditions, the only possible reaction is the electrolysis of the ester group to form pivalic acid and methanol, with a subsequent electrooxidation of the alcohol to produce H_2 and CO_2. Chronoamperometries (Fig. 2) at different potentials have confirmed that higher and stable currents could be achieved when the PEM cells work near 750 mV. The MP electrooxidation leads to a constant production of hydrogen at much lower potentials than in the case of traditional electrolysis of water, with a theoretical value of 103,6 $\mu mol.m^{-2}.s^{-1}$ calculated from Faraday's Law of Electrolysis.

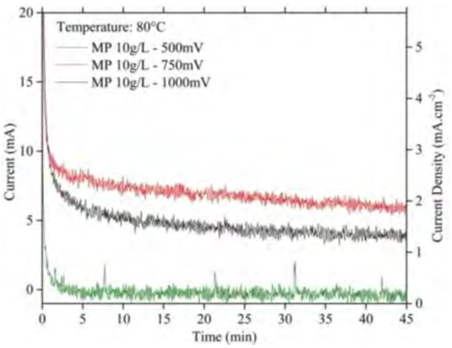

Figure 2. Chronoamperometry at different potentials for MP at 80ºC.

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SPM Studies on electrochemically deposited polydopamine films

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Polydopamine (PDA), a synthetic eumelanin polymer has gained interest in many research areas. PDA films are used as adhesive coatings for cell immobilization, for sensing, as coatings for energy-related research and as biomimetic electron gates for artificial photosynthesis due to its plethora of functional groups [1]. A widely used method for PDA deposition is dip coating by oxidation of dopamine in basic buffer solutions in the presence of oxygen or other oxidants [2]. An alternative method is electrochemical deposition via cyclic voltammetry or pulse deposition. For many applications, the film morphology, thickness and electrochemical properties are crucial and require controllable and reproducible depositions. In addition, the surface properties of PDA films can be altered by external parameters such as applied potential or pH, which plays a role in various applications.

Within this contribution, we present scanning probe microscopy techniques as useful methods to characterize PDA films in respect of the film morphology, film thickness and electron transfer behavior depending on the number of cycles or pulses applied during electrodeposition [3]. Scanning electrochemical microscopy (SECM) is a powerful technique to investigate heterogeneous electron transfer rate constants of modified electrodes using approach curves (**Fig. 1A**) [4]. PDA deposited on gold substrates are investigated with respect to electron transfer kinetics by applying different substrate potential or at different pH values. Using atomic force microscopy (AFM) contact mode the film morphology and film thickness (**Fig. 1B**) is determined in dependence of the applied number of cycles or pulses. Also, adhesion properties of PDA film in dependence of surface groups obtained by AFM force spectroscopy will be discussed.

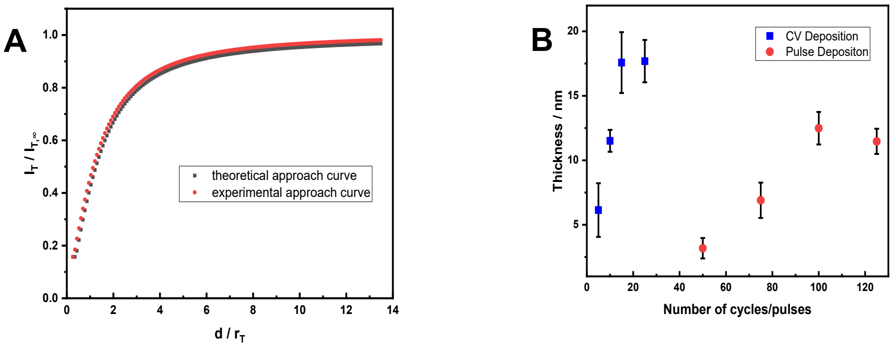

Fig. 1. **A** CV recorded in 5 mM hexaammineruthenium (III) chloride and 0.1 M KCl. **B** Thickness of the PDA films in dependence of number of cycles/pulses obtained by contact mode AFM.

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Development of Precise Pressure-Control Unit Equipped Compact PEM Water Electrolyzer for Catalyst Evaluation

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Introduction

For the low-carbon society, the hydrogen production using the renewable energy is essential technology. The proton exchange membrane water electrolysis (PEMWE) is one of the candidate methods in several water electrolysis. In the development of PEMWE, the performance evaluation of synthesized catalyst is indispensable factor. The precise performance evaluation of membrane electrode assembly (MEA) and the anode and cathode polarization measurement using the reference electrode is the essential factor for the catalyst evaluation. In this study, the small-size electrode electrolyzer was developed, which can precisely control the pressure to the electrode area, and measure the anode and cathode polarizations by the equipment of two reference electrodes for the anode and cathode side surface of PEM. The electrochemical measurements using these functions were performed.

Experimental

The electrode size of developed electrolyzer was 1×1 cm^2. The first feature was that this electrolyzer has the precise pressure control structure to the only electrode area, and the second future was that the two reference electrodes, which connected at the faces of anode and cathode sides on PEM, was equipped in the electrolyzer as shown in Figure 1. The MEA was fabricated by the transcription method. The anode and cathode catalysts and PEM used IrO_x (ELC-0110, TKK), Pt/C (TEC10E50E, TKK) and Nafion®117 (DuPont), respectively. The electrochemical measurements performed for the chronoamperometry (CA, 1.3-2.5 V), the electrochemical impedance spectroscopy (EIS, frequency; 10 k-1 Hz, amplitude; 10 mV) and the linear sweep voltammetry (LSV, 1.0-2.5 V, scan rate; 4 mV s^{-1}).

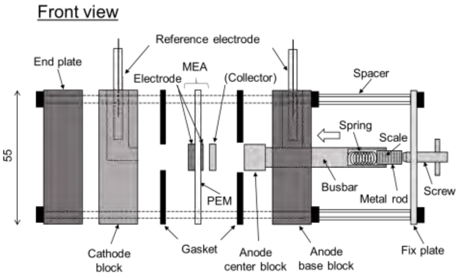

Figure 1 The structure of developed compact PEM water electrolyzer.

Results and discussion

The developed 1 cm^2 electrolyzer was compared with the conventional 16cm^2 electrolyzer, and the difference of performance was 1.6 % for the cell voltage at 1.0 A cm^{-2}. The optimized electrode-pressure as the specific value for developed electrolyzer-component was 0.52 MPa. Figure 1 shows the polarization measurement using two reference electrodes. The sheet resistivity of Nafion 117 using this method showed a 0.26 Ω cm^2, which was close to the reported-value [1]. The anode and cathode polarization curves, which were *iR*-corrected by PEM sheet resistivity, showed the linear tendency in Tafel plot. As a result, it was showed that this polarization measurement was the reasonable method as the polarization measurement of the anode and cathode reactions.

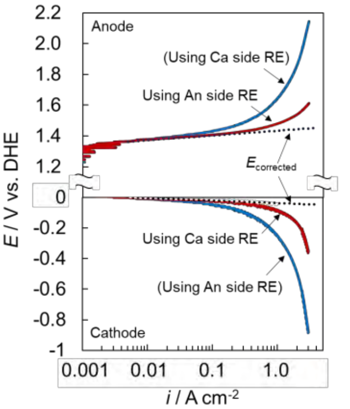

Figure 2 The anode and cathode polarization carves using two reference electrodes.

Acknowledgements

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Selective Electrooxidation of Glycerol on Mixed Nickel Cobalt Boride Embedded in a Polybenzoxazine-derived Nitrogen-doped Carbon Matrix

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The oxygen evolution reaction is one of the major factors that limit economically feasible water electrolysis on a large scale. Not only it necessitates a substantially higher overpotential than the hydrogen evolution reaction, but also produces already abundantly available oxygen, a not highly valuable product.[1]

Glycerol is a well-known non-poisonous reducing agent. An increasing demand for biodiesel has led to its excess supply and low price on the global market. It offers three possible oxidation sites and thus can be converted to a wide variety of products. Amongst them is lactic acid, whose bifunctionality as a hydroxycarboxylic acid makes it versatile for industrial application e.g. for production of biodegradable polymers and non-toxic esters. The substitution of water oxidation by glycerol oxidation (GOR) as the anode reaction in the water electrolysis process could hence make electrocatalytic hydrogen production more profitable in the future. In order to be competitive, electrocatalysts for GOR do not only need to be active and made from earth-abundant materials, but also be selective and stable.[2-3]

In this work mixed cobalt nickel borides were synthesized via wet chemical reduction of nickel and cobalt precursor salts by sodium borohydride and subsequent annealing at different temperatures in an inert gas atmosphere. To further improve catalyst stability and provide additional adsorption sites during glycerol oxidation, the catalyst was mixed with benzoxazine monomers (BO) in different mass ratios prior to the annealing step. The resulting cobalt nickel borides embedded in a N-doped carbon matrix were evaluated as electrocatalysts for glycerol electrooxidation using rotating disk electrode voltammetry in alkaline electrolyte. $(Co_{0.5}Ni_{0.5})_2B$/BO - with a catalyst:monomer ratio of 7:1, annealed at 500 °C - revealed increased activity as compared to the corresponding catalyst in absence of the benzoxazine-derived carbon matrix. Investigations on the catalyst selectivity and stability were performed using a flow-through cell set-up for up to 18 hours. The analysis of the reaction products by liquid chromatography indicated the presence of lactate in addition to other oxygenates from glycerol. Future experiments aim on further improving the selectivity towards lactic acid.[4-6]

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Cascade reactions in double confinement. Ag-Cu nanozyme-modified gas diffusion electrodes for CO_2 reduction

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The electrochemical CO_2 reduction reaction (CO_2RR) is a crucial technology for the formation of gaseous and liquid fuels and chemicals feed stock. So far Cu is one of the few catalysts able to perform C-C coupling at significant rates leading to longer chain carbon molecules. However, it requires high overpotentials and lacks selectivity. Bimetallic nanoparticles have shown improvement in selectivity for CO_2 to $C_{\geq 2}$ products taking the advantages of the two spatially closely located independent active sites. A first reduction of CO_2 to CO takes place at Ag and then this intermediate diffuses towards Cu, where the final products are formed, enabling the formation of $C_{>2}$ products at comparatively low overpotentials. The sequential transfer of intermediates across different sites in close proximity is called spillover catalysis.[1]

The Ag-Cu nanozyme (Fig. 1a) is one step forward in the design of catalysts enabling confined spillover catalysis. Its structure does not only place two different active centres in close proximity, but also creates a nano-confinement to increase the turnover on Cu. The nanozyme was designed to first produce CO at the Ag-core surface from where it is diffused into the porous Cu shell for further reduction. This tailored structure allows the formation of up to C_3 products at -0.6 V *vs.* RHE.[2] These results were achieved in an H-type cell, in which the formation rate of CO_2RR products are limited by CO_2 depletion, low current densities and competition with the hydrogen evolution reaction.[3]

Previous studies showed an improvement in the current density and the production rate of $C_{>2}$ when the same catalyst is introduced to a gas diffusion electrode (GDE) with CO_2 flow.[3,4] We herein present a strategy to combine these two advantages for an improved CO_2RR selectivity and current density. By dispersing Ag-Cu nanozymes into a GDE a double confinement environment is established. This is a result of placing the nanozyme catalyst at the gas-solid-liquid (three-phase) interface, allowing locally high CO_2 concentrations with minimal diffusional loss. By keeping the CO_2 concentration constant allows for an increased conversion rate and enhanced currents densities leading ultimately to an increased $C_{\geq 2}$ products formation rate alongside with a lower overpotential.

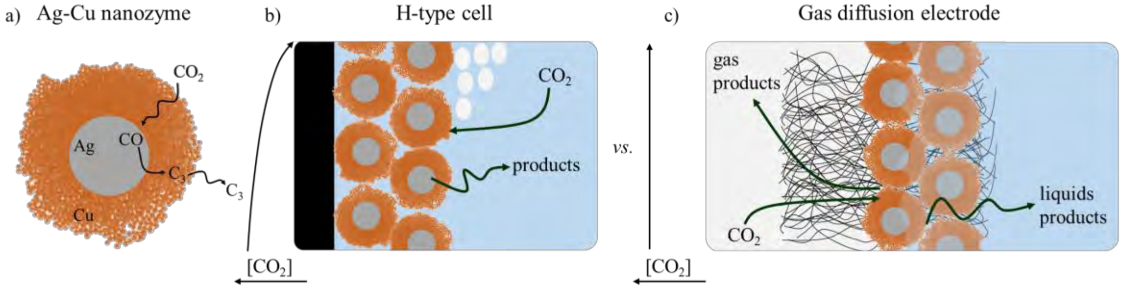

Figure 1. Schematic of the Ag-Cu nanozyme catalyst (a), H-type cell design (b) and the GDE electrode (c).

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On the border of electrochemistry and optics – studies of reaction products in a microcavity

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The main aim of our research is to couple electrochemistry with spectroscopic methods in a novel system made of a microcavity in an optical fiber (Fig. 1.)

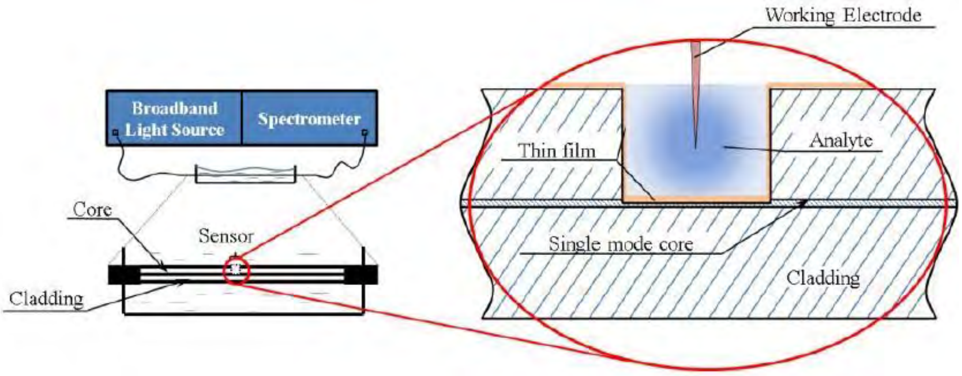

Fig. 1. Scheme of experimental setup – microcavity fabricated in an optical fiber

A microcavity fabricated in an optical fiber with the use of femtosecond laser has dimensions around 60 µm (length and depth) and acts as an electrochemical cell, in which picoliter volumes of solution can be analyzed, and simultaneously as an inline Mach-Zender interferometer.

We are preparing platinum microelectrodes, which put into microcavity play the role of working electrode. At their surface, electrochemical oxidation and reduction processes of studied analyte are carried out. The optical response to these processes is then examined, which gives more information about possible products.

We will compare the electrochemical response of the electrode inside the cavity with calculations in Comsol. We also present measurements of the optical response from the microcavity inline Mach-Zehnder interferometer recorded during electrochemical measurements.

Electrochemical fabrication of a LiZn-alloy – A two-step approach to reduce the volume expansion of alloy anodes

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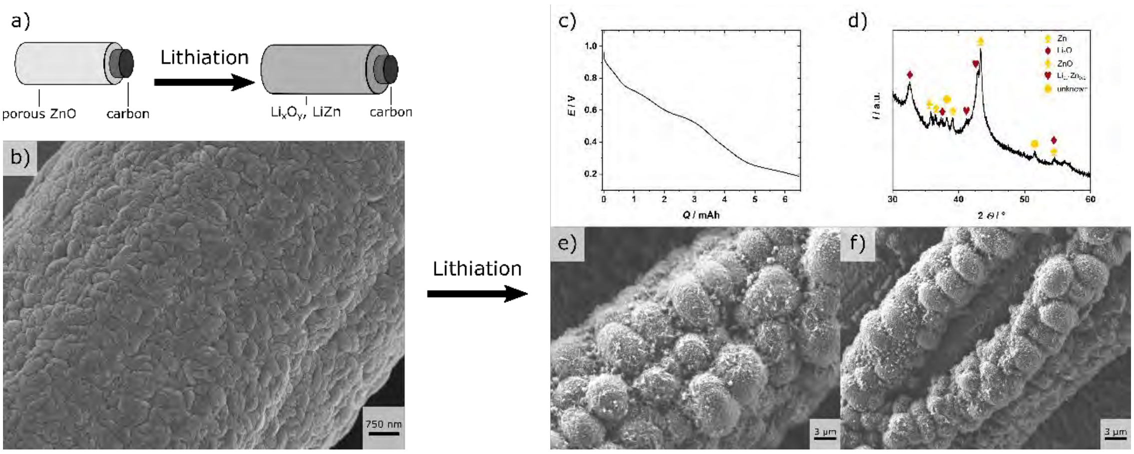
The current state-of-the-art electrochemical energy storage systems, i.e., lithium-ion batteries (LIB), reach almost their theoretical limit in energy density (584 Wh kg^{-1}).[1] Thus, the aim of current research is to increase the theoretical energy density. Especially the use of pure lithium anodes would lead to an immense increase in energy density due to the high specific capacity of lithium (3870 mAh g^{-1}). However, a lot of challenges hinder the commercialisation of pure metal anodes, *e.g.*, the growth of dendrites during metal deposition, which pose high safety risks.[2]

In order to build a bridge between safe and high capacity anodes, lithium-metal alloys are moving more in the focus of research.[3–5] In addition to the benefits, a number of challenges still need to be addressed, *e.g.*, the volume expansion and the contraction during lithiation and delithiation that can lead to cracking / deformation of the electrode.

Within this work we aim to reduce the negative effects of the volume effects using the example of a LiZn alloy. We thereby apply the alloy to a 3D-host structure (carbon mesh) over two steps (Figure 1 a). First, a porous ZnO-film is electrodeposited onto the carbon fibres of a carbon mesh. Afterwards, the ZnO-film is electrochemically converted into LiZn by reaction R 1.

$$\mathrm{ZnO} + 3\,\mathrm{Li}^+ + 3\,\mathrm{e}^- \rightarrow \mathrm{LiZn} + \mathrm{Li_2O} \qquad \textit{R 1}$$

First results indicate that ZnO is electrochemically converted into LiZn as intended. In the next steps, the LiZn@C-mesh is used as anode material in a LIB and the electrochemical reversibility is investigated by means of operando XRD. However, small cracks are still formed in the anode material (Figure 1 f). In order to decrease the negative effects of these cracks even further, ZnO nanorods[6] will be used in future experiments.



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Development of innovative electrolytes for potassium-ion batteries

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As one very promising post-lithium-ion battery candidate, potassium-ion batteries (KIBs) attracted the interest of researchers in recent years. Although potassium is much heavier than lithium or sodium, potassium-based batteries would reveal a number of advantages towards the lighter alkali-metal analogues. First, the half-cell potential of K^+/K can be even lower than the one of Li^+/Li depending on the used electrolyte composition [1]. Second, K^+ has usually a higher transference number within the electrolyte phase compared with Li^+ or Na^+ [1]. Third, potassium salts like KPF_6 are much less hygroscopic and can be produced at lower cost. And, in contrast to sodium ions, graphite is able to intercalate K^+ reversibly with a stoichiometric composition of C_8K (279 mAh g^{-1}) [2].

In this work we investigated the use of electrolytes based on 3-cyanopropionic acid methyl ester (CPAME) [3], tetraethoxy glyoxal (TEG) and tetramethoxy glyoxal (TMG) [4] for KIBs. From former studies, it is known that electrolytes based on these solvents display large electrochemical stability and are suitable candidates for the application in supercapacitors [3] as well as Li-ion batteries [4]. To the best of our knowledge, however, till now they have not considered in KIBs. The conductivity, viscosity, density, electrochemical and thermal stability of these electrolytes have been investigated in detail and compared to that of the frequently investigated electrolyte based on KPF_6 dissolved in ethylene carbonate/ diethyl carbonate (EC/DEC). Furthermore, the use of these electrolytes in combination with $K_2Fe[Fe(CN)_6]$ (prussian white) based cathodes and with graphite or soft carbon based anodes have been considered. The results showed that these unconventional electrolytes are promising in view of the realization of high performance KIBs.

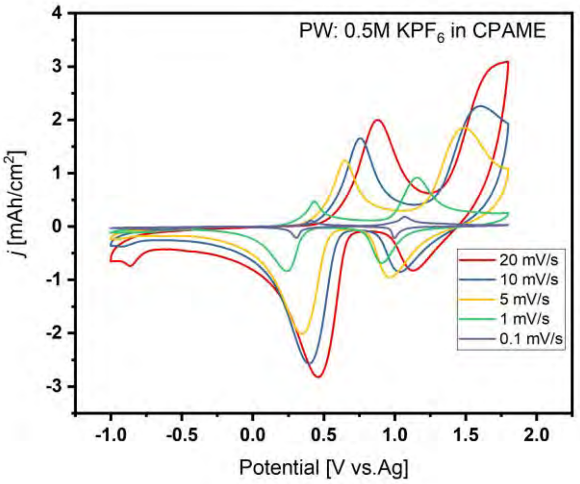

Figure: Cyclic voltammograms of $K_2Fe[Fe(CN)_6]$ at different scan rates. 3-cyanopropionic acid methyl ester (CPAME) was used as electrolyte solvent.

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Dimensionally Stable Anodes Using Titanium Substrates for Advanced Oxidation Processes

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Over hundred years, so many oxidation technologies have been developed in environmental engineering fields. Mostly, chemical and biological oxidation processes have been enough to treat organic and/or inorganic pollutants to meet the legal emission targets. However, recent wastewater including non-degradable organic compounds demands the development of advanced oxidation technology since non-degradable organic compounds are hardly decomposed by chemical and/or biological treatment technology. Particularly, discharge of toxic or highly concentrated industrial wastewater has been significantly increased due to rapid industrial development to be a serious water pollution. To overcome this problem, various water treatment technologies such as chemical oxidation, precipitation, adsorption, capacitive deionization, electrochemical oxidation and so on have been recently developed and introduced to industry. Among them, electrochemical oxidation of the compounds at anode is environmentally friendly, easily operated and maintained compared to conventional treatment processes. Nonetheless, cost reduction and enhancement of performance/durability of anodic electrodes are highly necessary for commercialization. In this study, $TiO_2/IrO_2/RuO_2$ electrodes that IrO_2 and RuO_2 coated on anodized Ti substrate were prepared and investigated in terms of various electrochemical properties.

Acknowledgement

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Ionic Connection between Anodic and Cathodic Catalyst Layers

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Most of electrochemically driven energy conversion devices consist of a pair of electrochemical reactions at electrodes and ion movement through electrolytes to complete full electrochemical cells. Ions move from anode to cathode or vice versa for electron exchanges. Pathway for ions is normally in an aqueous phase. Regardless, the introduction of any aqueous phase in energy conversion devices causes many problems during fabrication, operation, maintenance, and so on. Thus, much efforts have been devoted to develop quasi-solid electrolytes such as gel polymer, ion exchangeable polymers, impregnation of ions in porous matrix and so on. An approach to minimize areal resistance of film-type polymeric electrolytes is to make membrane thickness as thin as possible. Thus composite membranes have been highlighted as a new type of electrolytes. Composite membranes are made by impregnating polymeric electrolytes into thin porous substrates. However, hydrophilic ionomer is hardly impregnated into hydrophobic substrates. In this study, three-layered (electrolyte-skeleton/electrolyte-electrolyte) composite membranes with the thickness of 20-50 μm were prepared using porous substrates of various thicknesses. A technique to impregnate ionomer into hydrophilically treated porous substrates were developed so as to prepare void-free composite membranes. Characterization in terms of ion conductivity, ion exchange capacity, water uptake, dimensional stability, mechanical strength was carried out.

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Formation of Durable Triple Phase Boundary in Porous Catalyst Layers

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Energy conversion devices such as water electrolyzers or fuel cells require the movement of ions generated and consumed at two electrodes, i.e., anode and cathode. Ions should be transported inside electrodes to participate in anodic and cathodic reactions. Ion pathway is normally in liquid electrolyte. Regardless, the introduction of any aqueous phase in energy conversion devices causes many problems during fabrication, operation, maintenance, and so on. In addition, if gas penetration or gas evolution is one of phenomena taking place at electrodes, the electrodes should be porous. Thus, much efforts have been devoted to develop quasi-solid electrolytes such as gel polymer, ion exchangeable polymers, impregnation of ions in porous matrix and so on. Among the candidates, ion exchangeable polymers are quite often chosen as ion conducting media for energy conversion devices. The technique to introduce ion exchangeable polymers within electrodes for oxidation and reduction reactions is to solidify catalyst inks consisting of electrocatalyst, dispersion of ion exchangeable polymers, controlling solvents and additives by evaporation of all solvents in catalyst inks. Ion exchangeable polymers could be dispersed in various solvents. It causes different shapes of ion exchangeable polymers in solvents, for instance, cylindrical rods, a less-defined large particles, coils and so on. Such different types of ion exchangeable polymers form distinguished structure catalyst layers. In this study, the effect of solvents dispersing ion exchangeable polymers on the performance and durability of catalyst layers was investigated. Electrochemical characterization such as I-V polarization, cyclic voltammetry, impedance and so on and microscopic characterization such as SEM and TEM were carried out to evaluate the performance and durability of catalyst layers.

Acknowledgment
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Understanding the Effect of Porosity in Biomass-derived Carbon Electrocatalysts for CO_2 Reduction

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Electrochemical CO_2 conversion is a promising method to use renewable energy and waste CO_2, that otherwise would have been emitted into the atmosphere, and produce fuels and bulk chemicals.[1] Biomass-derived carbon electrocatalysts have triggered a considerable attention recently due to their excellent electrocatalytic performance, highly abundant resource, relatively low costs and good long–term durability.[2] Moreover, protein(heteroatoms), vascular bundle(tunnel), and inorganic salts(templates) present in the biomass source can modify the charge distribution and morphology of the carbon materials, resulting in enhanced electrocatalytic performance.

In a typical heterogeneous electrocatalytic reaction involving a gas reactant, the catalytic efficiency is limited by mass transport limitations of the reactant and the complexity of the reactions at the three-phase electrochemical interfaces (e.g., gas, solid, and liquid three-phase interfaces). In these cases, porous electrode structures with a high number of pore sites can promote a catalytic reaction at the interface, electrolyte ion diffusion and electron transport. Previous research has demonstrated that the optimization of the pore structure, including specific surface area, pore volume, pore size, and pore size distribution, is a highly effective approach to improve the electrocatalytic performance of biomass-derived carbon-based materials for CO2RR (CO_2 Reduction Reaction).[3] However, the difference in biomass sources, activators, preparation methods and conditions, bring different electrochemical performance, making it impossible to judge the specific functions of different porous structures in the electrochemical CO_2 reduction process.

Here, we designed a series of systematic experiments to explain the functions of porous structure in different bio-based carbon catalysts. The biomass-derived carbon catalysts were produced by a one-step method, using the same preparation procedure but altering activators. The textural analysis, such as: specific surface area, pore size distribution, degree of graphitization, etc. is combined with an analysis of the electrocatalytic performance (overpotential; product selectivity; current density and durability) towards CO2RR. From this study, we will show how the porous structure of biomass-derived carbon affects mass transfer during the electrochemical reduction of carbon dioxide. Finally, we will obtain an understanding of the role of different activators and the function of porosity in the CO2RR on biomass-derived carbon materials.

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Direct electron transfer of oriented bilirubin oxidase on three-dimensional carbon paper with reduced graphene aggregation

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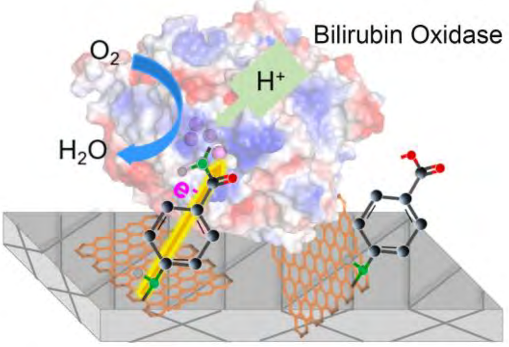
Aggregation of reduced graphene oxide (RGO) due to π-π stacking is a problem, as aggregation decreases the effective RGO working area.[1-2] Dispersing RGO on three-dimensional (3D) carbon paper electrode is one strategy towards relieving aggregation, but some aggregation still remains.[3] In this report we describe a study, where a negatively charged molecule 4-aminobenzoic acid (4-ABA) is grafted onto the graphene-based carbon paper electrode surface to induce orientation of the blue multi-copper enzyme *Myrothecium verrucaria* bilirubin oxidase (BOD) favourable for direct electron transfer (DET) for the oxygen reduction reaction (ORR) at neutral pH, Scheme 1. Simultaneous electroreduction of GO to RGO and surface grafting of 4-ABA are achieved by applying alternatingly negative and positive electrochemical potential pulses, resulting in very high catalytic current density (Δj_{cat}:193 ± 4 μA cm^{-2}) under static condition. Surprisingly we found that electrochemically grafted 4-ABA not only favours proper orientation of BOD validated by numerical model fitting to the electrocatalytic currents. RGO aggregation is also alleviated as disclosed by scanning electron microscopy, probably due to the electrostatic repulsion between the 4-ABA grafted graphene layers. Further, the bioelectrode shows outstanding operational stability with a half-lifetime of 55 h. Such a degree of stability has not been reported before. The bioelectrode is finally exploited in a gas diffusion configuration, offering great potential for applications for bioelectrochemical devices such as biofuel cells and biosensors.



Scheme 1. Schematic illustration of the prepared BOD on 4-ABA functionalized RGO-carbon paper electrode and its bioelectrocatalysis process. A possible orientation of MvBOD (PDB:2XXL), with surface charge distribution indicated with blue and red colour symbolizing positive and negative charges, respectively, is proposed (not drawn to scale). The left 4-ABA linker forms an amide bond with BOD, while the right 4-ABA with free –COO^- is still unreacted.

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Quantum dots on electrodes for a parallel read-out of biochemical reactions

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Semiconductor nanoparticles (quantum dots - QDs) have become attractive tools in bioanalysis because of their optical and electrochemical properties. This is related to applications using fluorescence, electrochemiluminescence or photocurrent generation [1]. For photoelectrochemical systems QDs are immobilized on conductive electrodes. By illumination electron-hole-pairs are formed inside the nanoparticles which can be used for photocurrent generation. Signal chains can be constructed when suitable donor or acceptor molecules are present in solution. The special feature of such electrodes is that the response is triggered by illumination of the sensing surface [1]. In this study, a light-switchable photoelectrochemical sensor was built by coupling QDs with two different oxidases to detect the respective enzyme substrates in parallel.

For this purpose CdSe/ZnS QDs have been immobilised via a dithiol compound on gold electrodes. Two different enzymes, glucose oxidase (GOD) and sarcosine oxidase (SOD) have been deposited on this QDs-electrode at spatially well resolved places. Here small spots can be achieved. A laser beam is moved over these spots to allow photocurrent generation. Since oxygen can act as electron acceptor at the illuminated QDs the photocurrent is correlated to the oxygen concentration near the surface. By action of the enzymes in the presence of the corresponding substrate a competitive situation for oxygen is created in front of the QD layer and thus, the photocurrent decreases [2, 3]. Since this occurs in a concentration dependent manner, analysis of the enzyme substrate is feasible.

Due to the spatially separated immobilisation of two oxidases, an independent read-out of the two enzyme reactions is feasible. The experiments indicate good lateral resolution and selectivity of the multi-detection system without any crosstalk between the two sensing regions and without any response at regions, which are not modified with an enzyme [4].

Furthermore, the possibility of an imaging of the enzyme spot by photocurrent measurement has been investigated. When the laser is moved over the spot of GOD with a constant speed, the size of the spot can be determined from the photocurrent - time curve (with a defined moving speed). The photocurrent correlates to different local enzyme activities. Consequently, an imaging of the enzyme activity distribution on the surface has also been achieved by this method.

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Photo-Induced Electrochemiluminescence at Semiconductor Electrodes

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Electrochemiluminescence (ECL) is a light-emitting process and a powerful tool in analytical chemistry. This phenomenon is induced by the excited state of a luminophore, which is generated by an electrochemical reaction at an electrode surface.[1] Conversely, photoelectrochemistry on illuminated semiconductors is a process where an electrode absorbs light, and that can be used to decrease the potential required to trigger an electrochemical reaction.[2] In this communication, we will introduce the photo-induced electrochemiluminescence (P-ECL) of anodic ECL systems involving $[Ru(bpy)_3]^{2+}$ and a luminol analog (L-012). In this approach, the ECL emission is triggered by holes photogenerated in an *n*-type semiconductor electrode, which is normally highly challenging due to competing photocorrosion occurring at semiconductor electrodes in aqueous electrolytes.[3] In a first example, we will present the results we obtained on Si-based tunnel electrodes protected by a Ni stabilizing thin films and demonstrate that these photoanodes allow generating P-ECL in water. We will show that, in this case, P-ECL can be used as an upconversion process where light absorption at 810 nm induces ECL emission (635 nm) at a record low electrochemical potential of 0.5 V vs SCE.[4] Also, recent results obtained using a UV incident light to induce simultaneously L-012 fluorescence and the formation of oxidizing holes in the photoanode suggest that P-ECL leads to a stronger emission than fluorescence and that this phenomenon can be employed to finely tune the overall luminescence.[5]

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Characterization of real-world electrocatalysts under operating conditions by soft x-ray spectroscopy: The EMIL@BESSY II *operando* infrastructure

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In context of the growing need for a more sustainable energy sector, catalyst materials research to improve water electrolysis and fuel cell (FC) electrodes plays a significant role in the transition to a green energy production. *In-situ* studies of promising electrocatalysts in conditions close to real operation is of crucial importance to understand the limiting mechanisms occurring in catalytic reactions. The combination of soft x-ray absorption (XAS) and emission (XES) spectroscopies is an established method that can probe the (local) chemical and electronic structure of solid, liquid, and gaseous samples from an atom-specific perspective, providing insights into their catalytic activity.

For this purpose, in the Energy Materials In-situ Laboratory Berlin (EMIL) at the BESSY II synchrotron facility, we have developed an infrastructure that allows XAS, XES, and RIXS (resonant inelastic x-ray scattering) studies of electrocatalysts under operating conditions. This setup is based on a 3-electrode electrochemical flow-cell attached to an ultra-high vacuum chamber (UHV) dedicated for *in-situ*/*operando* studies. The modular design of the electrochemical cell ensures project-specific upgrades besides the standard use with liquid electrolyte; for instance, the implementation of a microfluidic gas system that allows membrane-based designs for acidic water oxidation electrocatalysts or proton-exchange-membranes for FC applications. The system is installed at a two *undulator*-based beamline covering a probing energy range from the extreme ultraviolet (~80 eV) up to the hard x-ray regime (~10 keV). In combination with the high detection efficiency and (moderately) high energy resolution of the newly developed high-transmission soft x-ray emission spectrometer (HiTS), high-quality XES and RIXS spectra of all relevant elements can be collected at appropriately fast timescales i.e. several minutes, enabling measurements during normal operation of a myriad of electrocatalysts.

We present the current status of the instrumentation dedicated for *in-situ* characterization of real-world electrocatalysts under operating conditions at EMIL@BESSY II and the first *operando* experimental results on highly active iridium oxide-based oxygen evolution reaction catalyst.

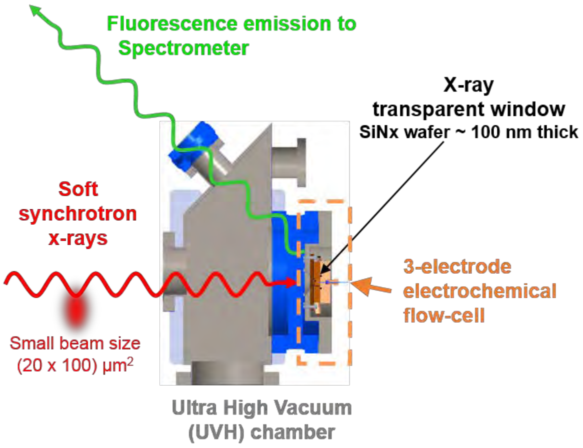

Figure: Schematics of the *operando* x-ray spectroscopy infrastructure at EMIL@BESSY II. The incoming x-rays generated at the synchrotron source impinge into the material through a thin membrane that separates the UHV environment from the examined material in the liquid electrolyte. The emitted fluorescence photons are collected with the energy dispersive spectrometer.

Towards *Operando* Studies of Electrolyte/Catalyst Interfaces in HT-PEMFC: Reference Materials Probed by X-ray Spectroscopies

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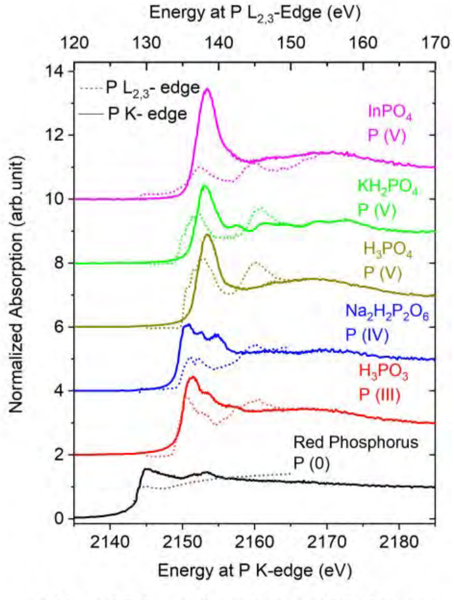
High-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) using polybenzimidazole (PBI) membrane doped with concentrated phosphoric acid are a promising candidate for a sustainable stationary energy source due to the promising combined heat and power efficiency[1]. However, long-term durability remains an issue and further optimization is needed to push HT-PEMFCs further into the market. By investigating the phenomena at the electrolyte/catalyst interface, light can be shed on the degradation mechanisms governing the lifetime of these devices. Several (*ex-situ*) studies have reported on the interaction between phosphoric acid-based electrolyte and Pt catalyst[2], but investigations dedicated to the reactions occurring at the electrolyte/catalyst interface under operating conditions are scarce.

We aim to elucidate the crucial interactions at the interface between H_3PO_4-based electrolyte and Pt catalyst by using *operando* absorption (XAS) and emission (XES) x-ray spectroscopy at the phosphorus K- and $L_{2,3}$-edge. Photon-in/photon-out x-ray spectroscopies are powerful tools to investigate the electrolyte/catalyst interface due to the detailed, element-specific information on oxidation state and local chemical structure that they can provide[3,4]. However, the interpretation of x-ray spectra can prove very intricate, since several phosphorus oxoacids might be generated when electric potential is applied to the Pt surface in contact with H_3PO_4[5], resulting in multiple and superposed contributions to the spectroscopic signal.

In order to pave the way towards *operando* investigations, a fundamental XAS and XES study on relevant phosphorus-containing compounds with different oxidation states and chemical environments has been performed at the P K- and $L_{2,3}$-edges. Complementary hard x-ray photoelectron spectroscopy (HAXPES) measurements have also been performed, and this unique dataset will facilitate the identification of the species emerging under operation conditions. Moreover, as an intermediate step towards real *operando* studies, differently prepared pellets containing Pt catalyst were immersed in aqueous phosphoric and phosphorus acid electrolyte and afterwards were probed at the P K-edge in order to gain insights into the electrolyte/Pt interaction at open circuit voltage (OCV).



P K- and P $L_{2,3}$- edge spectra of Reference Phosphorus Containing Compounds

As shown in the figure, both P K-edge and $L_{2,3}$- spectra are highly sensitive to the oxidation state and chemical environment of the different reference compounds, allowing use as speciation tools in the *operando* study.

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Simulation of Electrochemical Time-of-Flight Experiments in a Scanning Electrochemical Microscope for the Investigation of Electron-Transfer Reactions

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Reaction mechanisms in homogeneous catalysis using transition metal complexes often involve the formation of short-lived intermediates. To detect these intermediates, it is necessary to choose a technique with a short time-window relative to the lifetime of the investigated species. It has been shown that a scanning electrochemical microscope (SECM) can be employed to detect electrochemically active intermediates with short lifetimes and to investigate their electron-transfer kinetics [1-3].

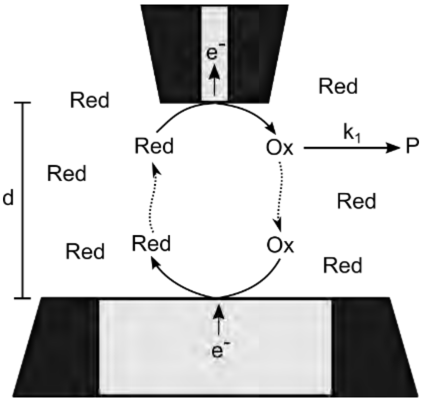

Figure 1: Schematic representation of the tip-generation substrate-collection (TG/SC) mode for the investigation of an E_rC_i-mechanism

In this contribution COMSOL Multiphysics was used to simulate electrochemical time-of-flight experiments using the tip-generation substrate-collection mode (TG/SC). A simple reaction mechanism of the E_rC_i-type was chosen as the basis of the simulation. As shown in figure 1 the oxidized species is generated at the tip-electrode via a heterogeneous electron-transfer and diffuses to the substrate-electrode where it is collected by electrochemical reduction. The collection efficiency depends on the distance *d* between the electrodes and the rate constant *k* of the coupled homogenous reaction. The simulation was used to explore the redox behavior of the species for varying tip-substrate distances and rate constants.

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Novel and Facile Synthesis of Cu$_{2\text{-}x}$S-Based Electrocatalysts for Selective CO$_2$ Conversion into HCOOH

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Formic acid is a valuable feedstock chemical that is utilized in broad industrial fields and is promising to be used in fuel cells.[1] The production of HCOOH or HCOO$^-$ via renewable energy driven electrochemical reduction of CO$_2$ is a promising strategy which combines renewable chemical synthesis, CO$_2$ emissions mitigation, and energy storage. Various materials have been investigated as promising electrocatalyst materials for selective and efficient CO$_2$ conversion into HCOOH (e.g., Sn, Pb, In and Cu$_x$S).[2,3] Among them, copper sulfide based electrocatalysts (Cu$_{2\text{-}x}$S) are promising candidates due to their activity, non-toxicity, and chemical abundance.[4] Moreover, the properties of Cu sulfides can be tuned by adjusting the stoichiometry, morphology, structure, and Cu valence state. Synthesis of Cu$_{2\text{-}x}$S particles with defined shape, particle size distribution, hierarchical organization, controlled stoichiometry, and defined crystal structure via a simple, low cost, and scalable process is still a challenge. Herein, we propose a simple, novel and inexpensive route for synthesis of digenite/roxbyite mixed phase cuprous sulfides via a direct reaction between elemental copper and sulfur dissolved in CS$_2$ and PhCH$_3$ at room temperature. The as-synthesized materials were characterized using variety of techniques including SEM, XRD, TGA/DSC and XPS. Electrochemically, the as-prepared materials showed that HCOOH is the only CO$_2$ER product (at < -1 V vs RHE in aqueous 0.1 M KHCO$_3$) and is produced with promising selectivity (55% FE). Additionally, we will provide our insight into the nature of the active site and the role of sulfur, and the subsequent mechanistic implications with reference to the conventionally described shift from carbophilic to oxophilic binding which characterizes the HCOOH production pathway.[4]

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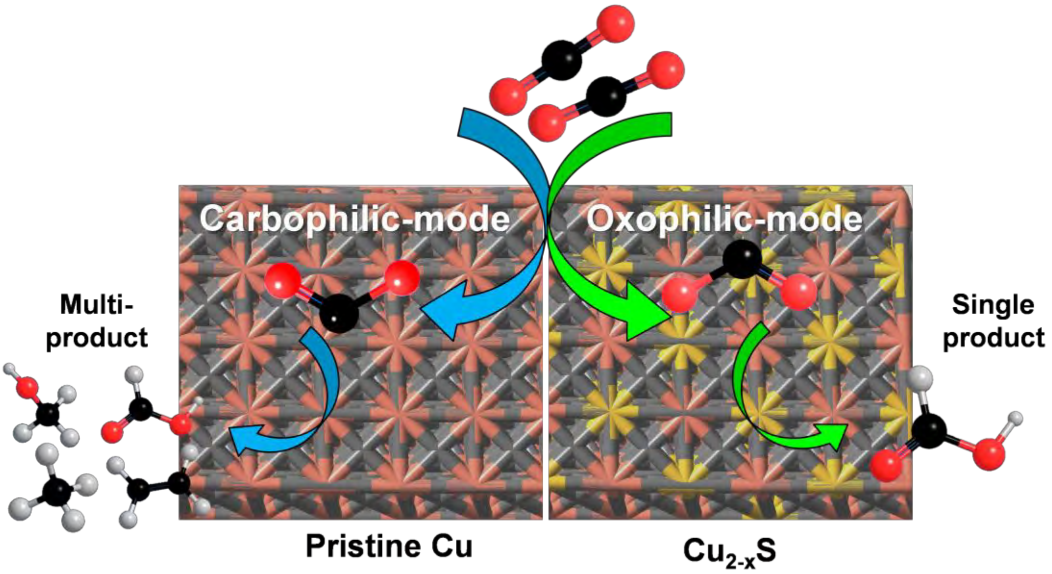

Electron-Hopping Governed Redox-Active Vertically-Aligned Mesoporous Silica Thin Films as Transparent Surfaces for Energy Storage Applications

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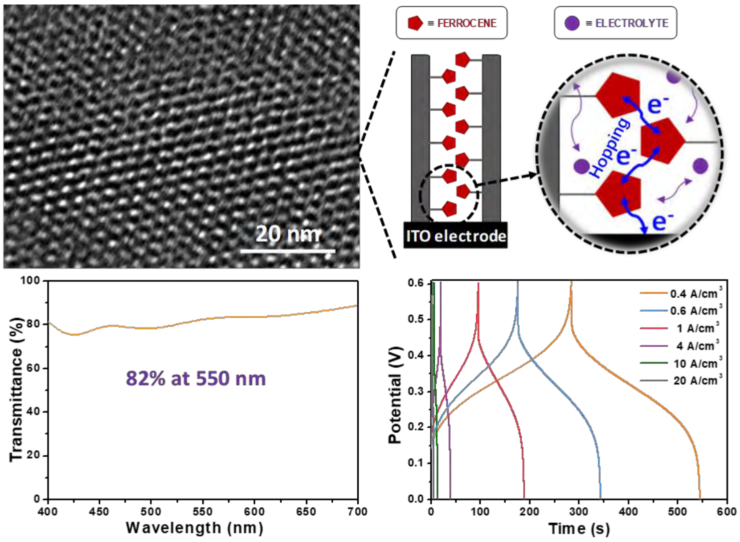
The slow redox reaction rates always restrict the power densities of faradic materials. Different from the conventional electron transfer mechanism, electron-hopping, namely charge transfer between close but isolated redox molecules, may have the potential to accelerate redox reactions.[1] However, large-scale spatial assembly of redox molecules to increase the energy density remains difficult, and few studies systematically evaluate the value of electron-hopping mechanism in the energy storage field. Therefore, organic-inorganic hybrid membranes made of a high density of redox active moieties covalently bonded to the internal surfaces of vertically-aligned mesoporous silica thin films have been prepared from the combination of an electrochemically-induced self-assembly method[2] (to generate azide functionalized silica) and a copper-catalyzed azide-alkyne click reaction[3] (to derivatize the material with electroactive groups such as ferrocene). In such rigid and insulating porous membranes, the charge transfer reactions take place through a pure electron-hopping mechanism between adjacent redox sites, which are favored by the ordered and oriented mesostructure containing large amounts of uniformly distributed ferrocene functions. The density of ferrocene molecules in the mesochannels can be controlled by adjusting the ratio of organosilane in the precursor solution and the relationships among the energy storage behavior, ferrocene density, and materials structure are analyzed in detail. The most effective system is the ferrocene-functionalized silica film prepared from 40% organosilane due to both high charge transfer rates (electron-hopping) and easy mass transport (fast diffusion of counter ions), which is able to deliver a capacity of 175 F cm^{-3} at the current density of 0.4 A cm^{-3}. (with up to 48% capacity retention achieved at a charging time as short as 2.8 s). Moreover, the very small thickness (105 nm) and the uniformly distributed vertical mesochannels with ultranarrow diameter (2 nm) also deliver 82% transparency at 550 nm, making the hybrid films promising energy storage materials for transparent devices.



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Electrochemical characterization of aptamers against a potential biomarker of pancreatic ductal adenocarcinoma

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Biomarker discovery is an active research area, especially in oncology. Cancer diagnosis still relies on invasive tumor biopsies that are not exempt from risks. In recent decades, the search for specific biomarkers which assist clinicians in diagnosing cancer and enable disease monitoring, selection of the appropriate treatment and early detection of recurrence, has enormously increased. Unfortunately, pancreatic ductal adenocarcinoma (PDAC) lacks suitable biomarkers that help improve the devastating survival rate due to a late diagnosis. In this disease, the stroma plays a relevant role as a physical barrier against drugs and as a promoter of the tumor formation, invasion and metastasis. Therefore, abnormal components of the extracellular matrix are regarded as potential targets for therapy and diagnosis. With the aim of identifying these components, specific receptors are needed and aptamers possess features that make them ideal for this task.

In this study, we were able to select DNA aptamers against a potential extracellular matrix component by designing a 4-round SELEX protocol on magnetic beads. Several sequences were selected for detailed characterization based on their sequence homology and secondary structure. Electrochemical bioassays on magnetic beads were used to estimate the binding constant of the aptamer-target complex formation. The best sequences showed dissociation constants in the nanomolar range similarly to other tumor biomarkers. Likewise, electrochemical inhibition experiments supported the affinity of the aptamer for its target in solution. Selectivity was assessed by aptahistochemistry in healthy and PDAC tissues, and by aptacytochemistry using different tumor cell lines with and without target expression.

Acknowledgements
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Construction and Characterization of a Flow Cell System in Comparison to the Rotating Ring Disk Electrode System.

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The generation of renewable energy fluctuates due to the intermittence of wind and sun. To have a stable energy grid, this energy has to be stored during highly productive days and released as needed. Electrochemical water splitting is attractive to store electricity in the form of hydrogen but limited by the slow kinetics of the oxygen evolution reaction (OER).[1,2] To understand this limitation, a mechanistic insight of the reaction is needed and can be gained using in situ spectroscopic studies on model electrodes. However, thin film model electrodes are difficult to integrate with commercially available electroanalytical instruments such as the well-established rotating ring disk electrode (RRDE) setup.[3] Furthermore, interfacing spectrometers with RRDEs is challenging. Therefore, we design a modular flow cell assembly that uses planar 5×10 mm electrodes and offers a simple interface with different spectroscopic systems. Our system can be adapted to various target reactions by changing the position, geometry and material of the electrodes as well as the flow geometry. The working and detector electrodes can be easily removed for post-mortem analysis. To validate our system, the redox behavior and mass-transport limitation were investigated using the ferri-/ferrocyanide redox couple in different electrolytes. Figure 1 shows the transport limitation as constant currents for both electrodes below ca. 0 V vs. SCE. The collection efficiency of the system in the mass-transport limiting case was simulated using multiphysics models in COMSOL®. The collection efficiency was found to be nearly independent of the flow rate at a value of around 35 %, which agrees with that calculated analytically.[4] The independence of the collection efficiency on the flow rate was also observed in cyclic voltammetry experiments using ferri-/ferrocyanide, where the collection efficiency was around 33(1) %, i.e. within 10% of the calculated value. The simulations have shown that products from the working and counter electrodes do not mix at experimentally used flow rates between 0.5 and 8 ml/min. In comparison to the RRDE system, we found that large flow rates are needed to produce the limiting current densities of typical RRDE experiments and that the time delay between production of the species and detection is larger in our flow cell. In conclusion, we find that our modular flow cell is a suitable alternative or addition to the common RRDE setups due to its flexible design and easy integration with further analysis systems to increase the information density of the measurement in future work.

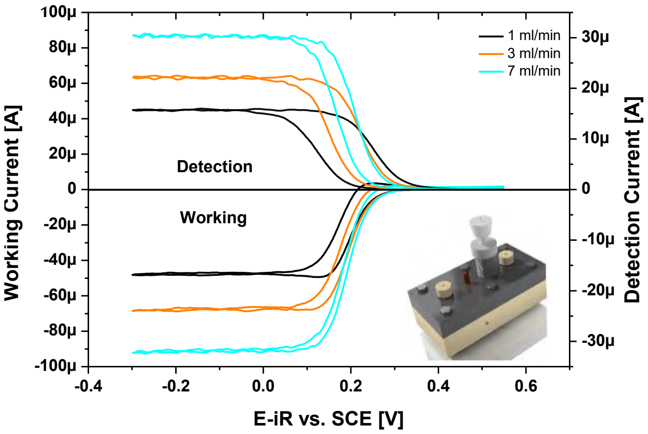

Figure 1. Collection efficiency measurements of the modular flow cell.

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Membraneless microfluidic fuel cells with increased power density by passive flow control

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Microfluidic fuel cells are considered as the most promising candidates for power sources in portable electronic devices [1-3]. In membraneless microfluidic fuel cells, fuel and oxidant flow in parallel at low Reynolds number without convective mixing. The membraneless architecture eliminates many of the problems encountered with PEMFCs. However, it is still difficult to commercialize microfluidic fuel cells, because at practical flow rates and useful cell voltages poor fuel utilizations below 10% and low power densities persist problematic [4]. This is mostly caused by the formation of concentration boundary layers at the electrodes. A possibility to reduce the thickness of the concentration boundary layers is to increase the flow rate. However, this results in a further decrease in fuel utilization. A simple alternative method for the suppression of the concentration boundary layer expansion is a passive flow control by using a curved microchannel, which induces a transversal secondary flow as sketched in Fig. 1b) [5]. The generated counter rotating vortices enhance the transport of fresh reactant from the center of the channel to the concentration boundary layers. In order to investigate the correlation between the current density and the transversal secondary flow, a fuel cell with a U-shaped microchannel was fabricated (Fig. 1a). Segmented electrodes on the top and bottom of the microchannel enabled an electrochemical characterization of the fuel cell within the straight and curved channel part. In addition, optical flow measurements were conducted using astigmatic particle tracking velocimetry (APTV) [6]. Besides the experiments, numerical simulations demonstrate that, using a curved microfluidic fuel cell the current density increases compared to a fuel cell with only a straight section, due to the induced counter rotating vortices (Fig. 1c) [5]. The higher the flow rate, the higher the current density. At a flow rate of 30 ml/h the current density increases about 8%, while at a flow rate of 100 ml/h an increase of more than 30% is achieved. Further results, including measured polarisation curves and APTV flow measurements will be presented and discussed at the conference to emphasize the correlation between fuel cell efficiency and the flow physics based on our experimental findings.

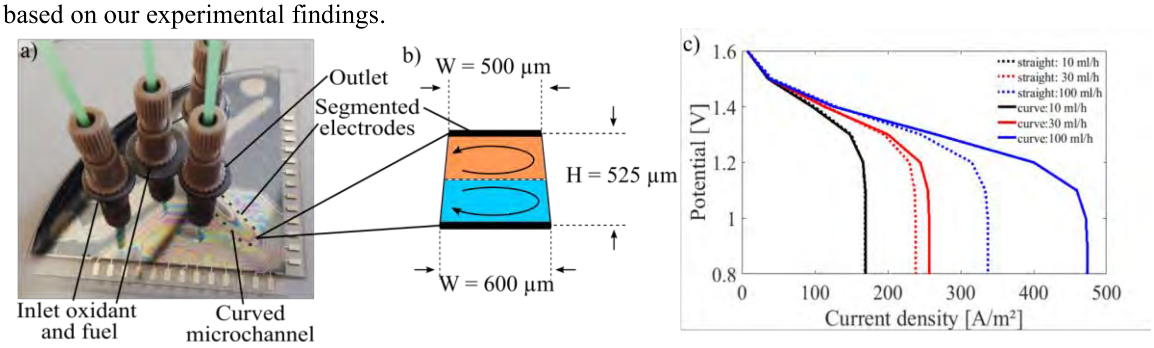

Figure 1. a) Photograph of the microfluidic fuel cell with segmented platinum electrodes on the top and the bottom of a curved microchannel. b) Cross-sectional view of the microchannel with sketched transversal flow induced in the curve of the channel. c) Simulated polarisation curves for straight and curved microfluidic fuel cell at three volumetric flow rates.

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MoO_3-CNTs Hybrid Material by Spray Coating and Electrodeposition as High Performance Negative Electrode for Supercapacitors

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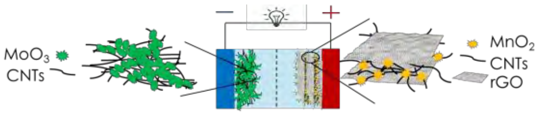
Combining transition metal oxides and nanostructured carbon materials is considered as one of the best strategy to achieve high performance supercapacitors electrodes [1]. Here is reported a novel way to increase energy densities while maintaining high power densities of supercapacitors exploiting pseudocapacitance and nanostructuration of electrode materials.

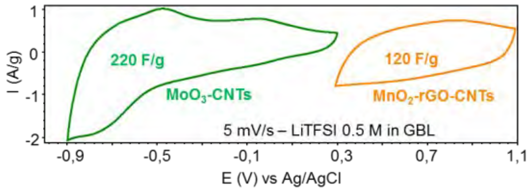
MoO_3 has been recently reported as an appropriate pseudocapacitive anode material with a high capacitance [2]. Carbon nanotubes are used for their high electrical conductivity and rapid charge storage kinetics. The challenge is to assemble both material in a homogeneous nanostructured electrode with controlled composition and structuration aiming to create a synergetic effect between both charge storage mechanisms to improve electrochemical performances.

First, MWCNTs are deposited directly onto a current collector by dynamic spray-gun deposition. This deposition method used for nanostructuration of thin films insures the formation of homogeneous mats with tunable thickness [3]. This method is reproducible, easily scalable and low-cost considering that it is compatible with large surfaces. Then, molybdenum trioxide is deposited by a cathodic electrodeposition method directly onto the nanostructured carbon framework formed by the carbon nanotubes. Electrodeposition is very versatile and allows a good control of the composition of the hybrid material and of the morphology of the metal oxide, both impacting the final electrochemical performances of the hybrid material. The mechanism of growth of this specific metal oxide is quite complex with several possible intermediates presenting different oxidation states depending on the environment [4]. We study the influence of deposition conditions (such as pH, concentration in Mo^{6+} ions, current density) on the physicochemical and electrochemical properties of the resulting composite material.

The composition and structure of this electrode material is characterized by SEM, XPS, Raman spectroscopy, and microporosity analysis. Influence of an additional heat treatment after the electrochemical growth on the performances of the material is studied as well. A great amelioration of electrochemical performances after treatment under air at 350°C can be noted and the capacitance of the final material can reach up to 220 F/g for this hybrid negative electrode in an organic electrolyte (LiTFSI at 0.5M in γ-Butyrolactone). Indeed solubility of the deposited MoO_3 has been found to be a major issue in aqueous electrolytes.

Finally a full asymmetric supercapacitor with two different metal oxide based hybrid materials using this particular organic electrolyte was developed, as can be shown in the figure below. A hybrid MnO_2-rGO-CNTs material presented in one of our previous publications [5] is used as the positive electrode. Performances of this hybrid system compared to a symmetric system based on carbon nanomaterials developed at our laboratory show a great gain in terms of energy densities from 5 to 25 Wh/kg with a power density of 100 W/kg when pseudocapacitive materials are added.





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Electrodeposition of Copper from Deep Eutectic Solvents – Influence of Composition

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Recently, there has been an increasing interest in the deposition of various metals from Deep Eutectic Solvents (DES) as an alternative to other non-aqueous electrolytes such as ionic liquids. DES typically consist of an organic (DES type III) or inorganic (DES type IV) salt in combination with a hydrogen bond donor.[1,2] If mixed in the eutectic ratio, they form a liquid due to freezing-point depression. Advantageous characteristics of DES include but are not limited to a rather low viscosity compared to ionic liquids, high conductivity, and a broad electrochemical stability window. Further, the two components are usually inexpensive and can be purified separately.[1-3]

Despite the extensive research in the field of DES performed over the last years, there is little knowledge about their thermal behavior.[4] This holds especially true for the impact of composition on the freezing point and the resulting freezing-point depression. However, this can influence the conductivity as well as the complexes present in the electrolyte, and thus the electrochemical behavior. In this study, we investigated the thermal and electrochemical characteristics of different DES as a function of their composition. The influence of the hydrogen bond donor, the salt, and their ratio is studied systematically.

Differential scanning calorimetry is applied to generate phase diagrams of DES type III and to determine the eutectic composition and eutectic temperature of the respective mixtures. The focus of the subsequent electrochemical characterization is on copper deposition as a model system. Investigated electrolytes are combinations of choline chloride or choline nitrate with hydrogen bond donors such as ethylene glycol or trifluoroacetamide. As a copper source, Cu(I) or Cu(II) species are added to the mixtures. An Au(111) single crystal is employed as a model electrode to study the initial stages of the copper deposition. Cyclic voltammetry, chronoamperometry, and the electrochemical quartz crystal microbalance are applied to elucidate the nucleation mechanism of copper on Au(111) from DES type III. Literature believes that high chloride concentrations influence the deposition.[5] Our study with choline nitrate suggests, however, that a high concentration of anions in general is crucial. The reaction mechanism of copper deposition also depends on the hydrogen bond donor, its ratio to the salt, and the copper species involved. In all media, deposition follows a nucleation and three-dimensional growth mechanism controlled by diffusion. The bulk deposition is probably preceded by underpotential deposition at more positive potentials.

Furthermore, we are applying these methods to copper-based DES type IV. Analogous to DES type III, these show a freezing-point depression and can be used as electrolytes in metal deposition. Because of the high concentration of copper salt, their deposition behavior in terms of the nucleation mechanism is different.

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Degradation of OER Based Reversal Tolerant PEFC Anodes – Innovative Characterization Methods and Further Insights

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Durability is a major lever for cost competitiveness of polymer electrolyte fuel cells (PEFCs) with respect to combustion engines for automotive and stationary applications.[1] The occurrence of cell reversal events due to gross fuel starvation in one or more membrane electrode assemblies (MEAs) can significantly reduce fuel cell lifetime. In this case, the increase in anode potential during cell reversals causes irreversible damage to the anode catalyst layer (ACL) and other PEFC components.[2,3]

The introduction of an oxygen evolution reaction (OER) catalyst, such as IrO_x, constitutes a material based mitigation strategy to reduce cell reversal induced degradation.[2–6] By lowering the activation energy of the water splitting reaction, the OER catalysts significantly reduces carbon corrosion during cell reversal.[7] To achieve increased lifetime and cost reduction, comprehensive understanding of degradation processes within reversal tolerant anodes (RTAs) is crucial for MEA manufacturing and material development.

In this work, a supported IrO_x catalyst is combined with a state of the art carbon supported platinum hydrogen oxidation reaction (HOR) catalyst. To facilitate fast and cost-efficient research, innovative characterization methods and procedures are developed for single cell ($< 50\ cm^2$) testing. A major focus is set on a cyclic combination of cell reversal and normal operation to characterize HOR and OER performance and interaction. The use of such a combination is still comparatively low [4], whereas state of the art accelerated stress tests (ASTs) focus on uninterrupted cell reversal testing. Therefore, focusing more on OER lifetime rather than normal operation lifetime estimation during repetitive, short-term reversal events occurring within automotive application.

Combining the developed AST procedure with advanced performance characterizations, such as hydrogen pump experiments, the individual contribution of mass transport, ohmic and HOR activation overpotential can further be quantified.

Besides the significant impact of using different HOR catalysts, a strong ACL structure dependency regarding the reversal tolerance was found (cf. Fig. 1). Using identical components and catalyst loadings, varying the ACL structure reveals a reversal tolerance increase by a factor of nine.

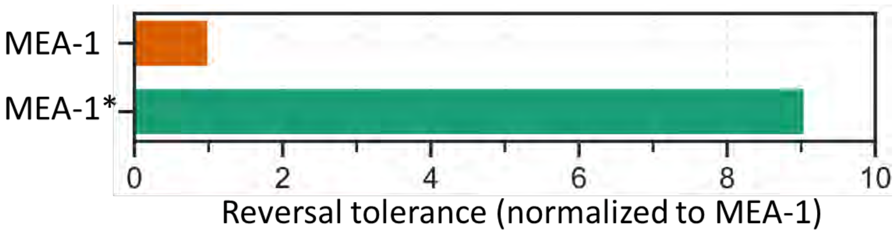

Figure 1: Reversal tolerance investigated by the developed cell reversal AST procedure for two different MEAs. Their ACLs differ regarding their structure whereas used components and catalyst loadings are identical.

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A Novel Multi-Functional Electrolyte Additive for Ni-Rich Cathode Materials

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Ni-rich layer oxides $Li[Ni_xCo_yMn_{1-x-y}]O_2$ ($x \geq 0.8$, NCMs) are promising advanced cathode materials for high-energy Li-ion batteries because of their high specific capacity (≥ 200 mAh g^{-1}) with an average discharge voltage of 3.8 V vs Li^+/Li, as compared to the commercialized cathode materials (e.g. $LiCoO_2$, $LiFePO_4$).[1] However, the instability of cathode–electrolyte interface causes the structural degradation of cathode active material and the electrolyte consumption, as well as gas evolution due to oxidative decomposition of electrolyte, resulting in a rapid capacity fading.[2]

Thus, improvement in the stability of cathode–electrolyte interphase is a key requirement to inhibit their structural degradation and enhance their electrochemical properties. The formation of a protective surface film *via* electrolyte additives is considered a cost-effective and reliable way to improve the cathode–electrolyte interfacial stability, as the stable surface film, uniformly distributed over the entire cathode surface, would prevent direct contact of oxide with the electrolyte, still allowing Li^+ transport between the cathode and electrolyte.[3] In this work, we report the high-performance NCM cathode through interfacial stabilization using a novel electrolyte additive. The details of surface film stability and formation mechanism, and their relation to gas evolution as well as cycling performance would be discussed.

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Pitfalls in Lithium Metal Battery Characterisation

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Since the early days of rechargeable battery research,[1,2] metallic lithium as an anode material has been considered a “holy grail” due to its highly negative potential (-3.04 V vs. SHE) and high theoretical capacity (3860 mAh·g^{-1}).[3] In the age of electro-mobility, exploiting the resulting high energy density of lithium metal has become even more desirable.[4]

However, even after intensive efforts in the last decade, lithium metal batteries (LMBs) still suffer from severe problems such as low cycling stability and low coulombic efficiency.[5] These performance shortcomings are mainly due to the high reactivity of the lithium metal towards electrolytes and dendrite formation during cycling. Major concern they cause is the safety of the LMB cells.

In order to tackle these issues, there has been growing consensus in the scientific community to aim for common reporting standards and testing conditions.[6] However, before these are established, it is necessary to understand the impact of the different experimental parameters on the trustworthiness of the testing results.

The aim of this study therefore was to investigate the influence of different experimental parameters, such as current density, amount of lithium metal moved, type, and quantity of electrolyte, in symmetric and asymmetric lithium metal cells. To better understand the morphology changes happening during lithium plating and stripping, complimentary techniques, such as *operando* dilatometry and *post-mortem* scanning electron microscopy, were used. We will discuss why potentially neglected parameters could have a significant impact on the outcome of measurements and in what way the findings of this study could be used to establish a reliable baseline for future LMB tests.

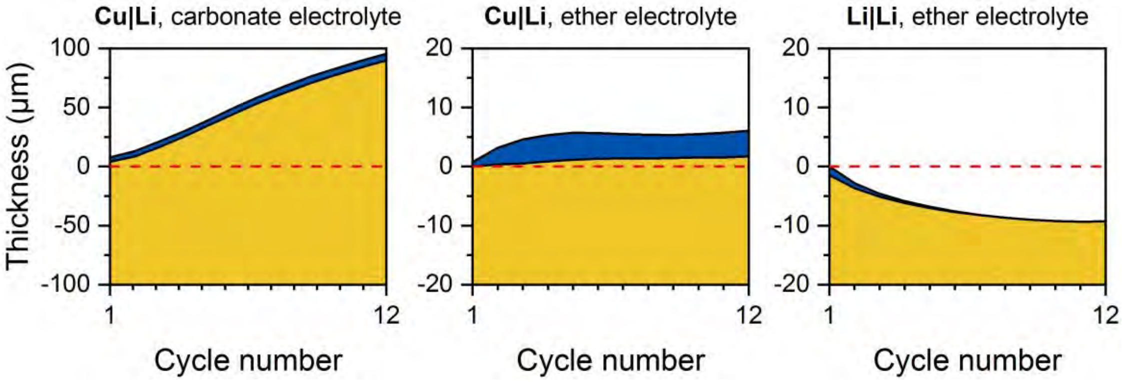

Figure 1: The thickness change of the working electrode (d = 7.5 mm) during cycling (2 mAh·cm^{-2}, 2 mA·cm^{-2}) can be positive or negative depending on cell configuration and electrolyte.

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Study of CO_2 Electrochemical Reduction Over CuO_x Nanoparticles Supported on Graphene-based Materials

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Capturing and converting CO_2 to easily storable fuels has become a hot research topic, in the last few years, due to its potential contribution to obtaining carbon neutral energy cycles. Among all the metals used for CO_2 electrochemical conversion, copper takes a special place; the main reason is related to its unique capacity of generating a wide range of CO_2 reduction products like HCOOH, CH_4, CO and promoting carbon–carbon coupling to obtain ethylene and ethanol. Copper electrodes have been extensively studied as electrodes for electrochemical CO_2 reduction reaction (CO_2RR)[1]. Nanoparticles, in particular, were reported to improve selectivity and increase energy efficiency. However, the choice of nanostructured supporting materials received only limited attention. Our aim was to study the effect of a graphene-based supporting material on copper nanoparticles stability and on products distribution.

We studied copper nanoparticle supported on two types of graphenide compounds. The first material was prepared from a graphenide solution obtained dissolving a nanocarbon intercalation compound of formula KC_8 in THF [2]; this solution act as a reducing agent for $CuCl_2$ salt, resulting in the precipitation of copper oxides nanoparticles over graphene sheets (Fig.1). The other material was an intercalation compound where copper nanoparticles are entrapped in between graphene sheets of larger dimension. XPS analysis confirmed the presence of copper (I) and copper (II), in agreement with what we found with the XRD analyses that showed reflections due to $Cu(OH)_2$ and Cu_2O phases.

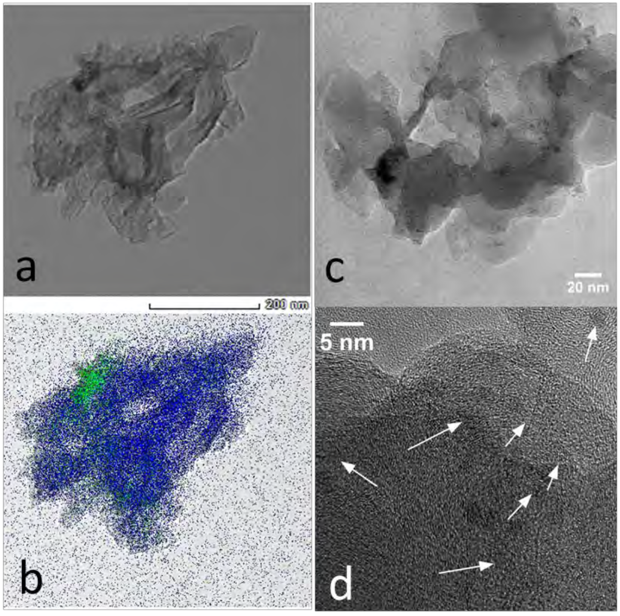

Fig. 1. (a) Lower magnification HR-TEM image of an aggregate of the CuOx(NP)/nC composite; (b) the corresponding EDX map; (c, d) Respectively lower and higher magnification HR-TEM image of the Cu(nP)/nC.

Powders were first suspended in an appropriate solvent, then dropcasted onto a glassy carbon disc and electrochemically reduced to metallic copper in situ before performing electrolysis.

Preliminary results showed that electrochemical reduction of CO_2 in a carbonate buffer at CuO_x(NP)/nC electrodes gave a formate yield close to 50%; higher than what reported for polycrystalline copper [3], to confirm the efficiency of nanostructures. The graphene intercalated copper oxide nanoparticles compared to surface anchored nanoparticles exhibit a very small activity but a better current stability for prolonged electrolysis (20 h). Using oxidation/reduction charge of copper oxides, obtained from cyclic voltammetries, we verified that we had negligible loss of material after prolonged polarization, even at potential where gas evolution on the electrode was massive.

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Platinized Ti and Black Titania Nanotube Electrodes prepared by Galvanic Deposition Methods

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This work aims at the preparation of Pt-coated Ti-based electrodes and their testing in the hydrogen evolution reaction (HER). Metallic Ti and black TiO_2 nanotubes (b-TNTs) were used as substrates. TNTs were annealed at 500°C in a vacuum quartz ampule, in the presence of CaH_2 powder to form anatase b-TNTs, which show high electronic conductivity [1]. Both substrates were pretreated before surface Pt loading; metallic Ti was etched in an acidic solution, whereas b-TNTs were subjected to electrochemical reduction-cathodization. Galvanic deposition [2,3] of Pt on both pretreated materials took place spontaneously in a $PtCl_6^{2-}$ ion solution; Pt(IV) complex ions were reduced-deposited as metallic particles on the pretreated Ti metal and b-TNT surfaces, while the freshly reduced substrate (etched Ti or cathodized b-TNTs) was partially re-oxidized. XRD measurements of the b-TNTs confirmed the preferred [001] orientation, which is highly desirable for improved electronic conductivity of the oxide. Top and cross sectional SEM/EDS observations show the distribution of the precious metal particles on the surface of both the metallic Ti and the b-TNTs. In both cases, cyclic voltamograms revealed Pt surface electrochemistry (*Figure 1a*), proving that the galvanic deposition method can also be applied to a partially reduced conductive oxide. Finally, HER in acid was studied by means of near steady state linear sweep voltammetry with a potential sweep rate of 5 mVs^{-1} (*Figure 1b*). Results at Pt/b-TNTs electrodes were compared to those of Pt/Ti electrodes and proved the latter to be more efficient HER cathodes.

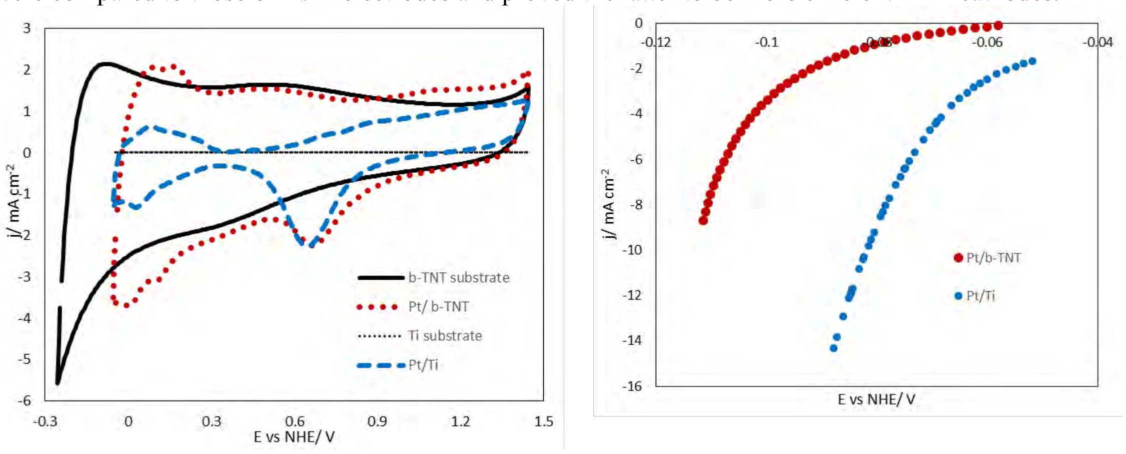

Figure 1 a. *Cyclic voltamograms of Pt/Ti, Pt/b-TNT and bare Ti and b-TNT electrodes, recorded at 50* mVs^{-1} *in a 0.1 M deaerated* $HClO_4$ *solution and* ***b.*** *HER activity of Pt/Ti and Pt/b-TNT electrodes, recorded at 5* mVs^{-1} *in a 0.1 M deaerated* $HClO_4$ *solution*

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Treatment of an industrial winery wastewater by anodic oxidation: a comparison between the DSA Cl_2, DSA O_2 and BDD electrodes

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Winery wastewater (WW) contains various organic and inorganic contaminants and its environmental impact is notable, mainly due to the large volumes produced and its seasonal variability **[1]**. The biological process requires large spaces and produces high quantities of sludge. In this context, electrochemical technologies represent a potential way to reach efficient elimination of organics from industrial wastewater. Anodic oxidation (AO) stands out among these processes. In this process, organic pollutants are completely mineralized to CO_2, water and inorganic salts by means of physisorbed hydroxyl radicals ($^{\bullet}OH$) **[2]**. The objective of this work was to compare the effect of three electrodes on the AO of the WW from a Chilean industry without the addition of salts (supporting electrolyte), at room temperature 25.0 ± 1.0ºC and at the original pH value (pH = 4). The electrolysis was carried out in an undivided 0.10 L open cell with always vigorously stirred to ensure the mass transfer. A Boron Doped Diamond (BDD) electrode, and dimensionally active anodes, one of chlorine and the other oxygen (DSA-Cl_2 and DSA-O_2) were used as anode. A stainless-steel cathode was used for each electrolysis. All the experiments were performed applying a current density of 30 mA/cm^2. The degradation of the organic compounds present in the wastewater was followed by spectrophotometric techniques and the mineralization was studied by removal total organic carbon (TOC).

Table 1. Parameters of WW treated by industrial biologic digestion and anodic oxidation

Parameters	Final industry effluent	AO (BDD)	AO (DSA Cl_2)	AO (DSA O_2)
Color	Uncolored	Uncolored	Uncolored	Uncolored
Total organic carbon (mg/L)	605 ± 41	225 ± 35	1610 ± 68	1300 ± 30
pH	7.30 ± 0.11	8.15 ± 0.10	4.22 ± 0.12	4.58 ± 0.20
Turbidity (NTU)	22 ± 0.20	12.80 ± 0.23	4.85 ± 0.20	6.73 ± 0.30
Abs. at 280 nm (U.A)	0.10 ± 0.08	0.37 ± 0.01	0.25 ± 0.13	0.25 ± 0.01
Conductivity (mS)	2.10 ± 0.30	2.73 ± 0.21	2.42 ± 0.32	2.82 ± 0.15
Mineralization energy (kW h/m^3)	-	279 ± 7.64	75 ± 0.01	134 ± 0.95
Mineralization cost by liter of solution ($USD)	-	48.90 ± 1.34	13.13 ± 0.01	23.51 ± 0.17

Table 1 shows that when working with the BDD electrode, the greatest degradation is achieved (86%). In addition, it is possible to achieve a degradation approximately 2.7 times greater than when the aerobic treatment is applied. However, it presents the highest mineralization energy. On the other hand, it is observed that the decolorization of the solution is dependent on the anode material used. In this context, absorbance decay reaches about 77% with DSA Cl_2 and DSA O_2 electrodes and 65% with BDD. However, in all cases an uncolored solution was obtained, these results are in concordance with the turbidity decay. This work demonstrated that AO can be successfully applied without the addition of supporting electrolyte, without adjusting the pH and at room temperature to remove the organic matter from wastewater produced by the wine industry.

Acknowledgments: We are grateful to, Associative DICYT project N° 021811HC_DAS, FONDECYT GRANT 1170352 and PhD fellowship N° 21170083 awarded to Y. Lauzurique-Guerra.

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Electrocatalytic activity of Au-Cu nanomosaic towards CO_2 reduction

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Since the consumption of fossil fuels increases as well as the deforestation, the level of CO_2 in the atmosphere is growing. Furthermore, it is well known that CO_2 is causing the expand of global warming effect and ocean acidification. Therefore, many efforts are undertaken to recycle carbon dioxide into carbon-containing fuels that can help solve both above-mentioned problems. The electrochemical reduction of CO_2 supported by solar radiation, seems to be an promising solution [1, 2]. Among others, such metals like gold, silver, copper or platinum were studied to obtain methane or methanol out of CO_2. Nevertheless, the combination of two metals can be an interesting alternative, especially when it comes to gold and copper. On one hand, Au is one of the most efficient catalyst for CO_2 reduction [3]; on the other one, Cu is selective towards production of hydrocarbons at relatively low overpotential [4]. Following that, in this work we present the unique approach resulting in the formation of stable bimetallic structure, namely Au-Cu nanomosaic.

Fabrication of nanomosaic onto structured titanium foil is based on the sequential procedure including: anodization, chemical etching of as-formed nanotubes, magnetron sputtering of thin metal layers and finally rapid thermal treatment. SEM inspection performed after chemical etching reveals the creation of regularly distributed dimples in Ti substrate that can act as host wells for guest metal species. As also confirmed by SEM analysis, Au-Cu nanoparticles or coatings are formed depending on the temperature of thermal annealing. UV-Vis absorption measurements show over 400 nm shift of the band maximum towards red as well as its broadening for bimetallic materials in comparison to the monometallic ones. The chemical nature of prepared electrodes were checked by XPS and the presence of diverse Cu species (Au-Cu alloy, CuO, $Cu(OH)_2$) was noticed. Moreover, the electrochemical activity of samples was characterized in dark and under electrode illumination in 0.1M $NaHCO_3$ saturated with Ar and CO_2. Obtained results strongly suggest that proposed in here material can be used for CO_2 photoreduction and since applied techniques are already available in industry, the facile scaling up of the whole fabrication process is reasonable.

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Ir/TiON$_x$/C High-Performance Oxygen Evolution Reaction Nanocomposite Electrocatalysts in Acidic Media: Electrochemical Activity Benchmarking Protocol

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Electrocatalysis plays an important role in the future transition to sustainable energy. The state-of-the-art electrolyzer catalysts for oxygen evolution reaction (OER) are based on iridium and its oxides, since they exhibit the optimal ratio between activity and stability. Because of the scarcity of this critical metal, a lot of efforts are invested in the development of new electrocatalysts materials, which would either be intrinsically more active with at least the same stability as Ir or would have improved utilization of Ir. Achieving the latter is directly related to the development of sufficiently stable and conductive supports. To increase the utilization, Ir has been supported on oxides, such as antimony tin oxide (ATO), indium tin oxide (ITO) and titanium oxynitride (TiON$_x$).[1]

Here we present a new Ir-based high-performance electrocatalytic nanocomposite for OER, consisting of Ir nanoparticles with an average size of 3–4 nm, effectively anchored on a titanium oxynitride support (TiON$_x$), which is distributed across a high-surface-area Ketjen Black carbon (Ir/TiON$_x$/C). We note that direct physical contact between iridium and carbon has been omitted in order to avoid carbon corrosion. Additionally, new variations of the material have been developed, where prior to the addition of Ir, various amounts of Cu were added to the support (Ir/Cu-TiON$_x$/C).

One of the unresolved questions in the OER community is how to adequately and reliably measure the activity of the new catalysts and compare them with the literature data. This is obviously due to the lack of unified benchmarking protocol. To study the effects of different parameters on the activity measurement, an investigation was made on a benchmark catalyst Ir black (Alfa Aesar). The impact of parameters, such as loading, activation protocol, backing electrode and catalyst ink composition was systematically evaluated.

Our findings present guidelines on how to measure intrinsic OER mass activity. By appropriate benchmarking of OER activity via reproducible measurements and with meaningful normalization, we can now accurately compare Ir black to our new Ir/TiON$_x$/C electrocatalytic composite and justly proclaim its superior activity.
The new Cu-doped Ir/Cu-TiON$_x$/C materials exhibited even higher activities. The effect of the amount of the added non-noble metal was studied. It was shown that the increasing amounts of Cu enhances the activity of the catalyst, however, exhibits some stability issues.

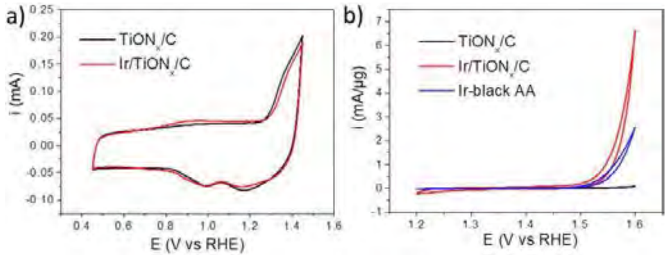

Figure 1: (a) Activation of TiON$_x$/C and Ir/TiON$_x$/C on Au electrode; (b) Activity for OER. Activation protocol: 0.45–1.45 V versus RHE, ink: 5 mlMQ + 3 ml Isop.[1]

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Enzyme functionalized AuNPs-TiND electrode towards glucose sensing

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Nowadays diabetes is one of the most dangerous civilization diseases. Above 400 million people are sick and additionally, that value is still growing [1]. The reason for this is an increased insulin level in the human body caused by a high carbohydrate diet in particular. Therefore, there is a need for sensors that can monitor the level of glucose especially in body fluids other than blood.

This work is intended to show the preparation method of the enzymatic biosensor as well as the characterization of its electrochemical properties. The electrode material was prepared starting from the anodization process of Ti foil. As a result, the TiO_2 nanotubes were created (Fig.1a). Then after the chemical etching, the Ti nanodimples(TiND) hidden underneath NTs were exposed (Fig.1b). Finally, the nanodimples were covered by Au film by magnetron sputtering (Fig.1c) and thermally treated in furnace (Fig.1d) and AuNPs-TiND was received.

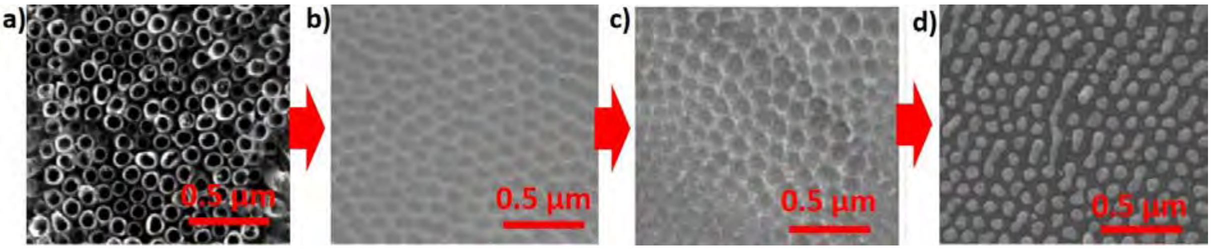

Fig. 1 The SEM images show all stages of material preparation: a) TiO_2 nanotubes, b) Ti nanodimples, c) Ti nanodimples covered by thin Au film, d) Ti nanodimples covered by Au nanoparticles.

Afterwards, the AuNPs-TiND material was modified by the enzyme [2]. The modification mixture consisted of three components: glucose oxidase (GOx), glutaraldehyde (GA) and bovine serum albumin (BSA). The chemical nature of functionalized material was characterized using X-ray photoelectron spectroscopy (XPS). Additionally, the complete coverage of the enzyme layer onto AuNPs-TiND was confirmed. The obtained electrodes were tested in 0.1 M PBS with an addition of glucose using cyclic voltammetry (CV). Basing on the series of CV measurements, the sensitivity of 25.74 $\mu A/cm^2 mM$, the linear range of 0.051-3.05 mM and the limit of detection equal to 7.61 µM were determined. These parameters ensures the successful glucose detection in human body fluids and therefore fabricated material can potentially find its application in developing fully operating sensor.

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$LiMn_2O_4$ – a model catalyst for the oxygen evolution reaction: the origin of the total current and the impact of oxidation on the OER in aqueous solution

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Controlling the oxygen evolution reaction (OER) is a crucial step for the long-time storage of electricity from renewables in chemical energy carriers.[1] Using $LiMn_2O_4$ as a model catalyst for this multi-electron transfer reaction, we aim to unravel the influence of bulk manganese valence state on the performance of catalytic water oxidation.

Using nano-size $LiMn_2O_4$ particles in a rotating ring-disk electrode (RRDE) setup, we identified the detection potentials of oxygen and manganese in separate calibration experiments to evaluate the catalytic performance and activation of our catalyst in a sodium hydroxide electrolyte (pH 13). Our analysis confirmed that total current per electrochemical surface area (ECSA) is the sum of the oxygen evolution and manganese loss at the investigated reference voltage. Additionally, we calculated an average Faradic efficiency of 75% after the electrode reached steady state after five cycles. The initial decay of disk current was assigned to manganese loss, while fairly constant oxygen evolution is detected at the ring (Fig. 1).[2]

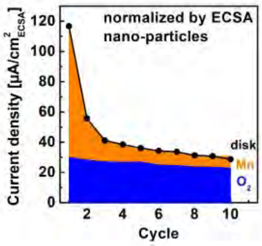

Figure 1. Calculated assignment of the currents due to Mn loss (orange) and catalysis (blue) to the measured disk current in NaOH for nano sized particles.[2]

The $LiMn_2O_4$ behaved differently in LiOH[3] electrolytes than in NaOH.[2,4] Definite redox peaks in the LiOH electrolytes with a concentration below pH 14 indicate manganese oxidation during rotating ring-disk electrode (RRDE) experiments that is more distinct at lower pH and Li^+ concentration. This pH-dependent oxidation of the active material was confirmed by X-ray absorption spectroscopy (XAS) of post mortem electrodes and has a disastrous effect on the onset of the OER causing an increase of the overpotential in less concentrated LiOH electrolytes and an unexpected non-zero Nernst slope (dE/dpH) of -40(4) mV/pH.[3] A E^{RHE}-pH diagram based on a thermodynamic model of $Li_xMn_2O_4$ lithiation and delithiation (Fig. 2) agrees with the experimental data and gives the same Nernst slope of delithiation of 116(25) mV/pH.[3] Thus, we believe that the observed oxidation is due to delithiation of the catalyst in aqueous solution. Our conclusions and the graphical representation of stability against redox changes may be useful for other battery materials that are increasingly used as electrocatalysts. It is crucial to get a better understanding of catalyst stability in different pH as it can change its catalytic properties.

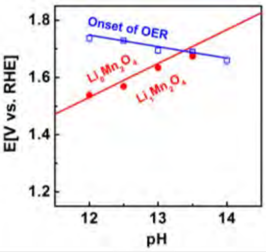

Figure 2. E^{RHE}-pH diagram of $LiMn_2O_4$ showing the boundary line of delithiation and the onset of the OER in LiOH.[3]

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Electrocatalysis at the Liquid/Gas Interface: The Gas Accessible Membrane Electrode (GAME) for High-rate Reactions and In-Situ/Operando Characterisation

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Electrocatalysis plays a significant role in energy storage devices, such as fuel cells and water electrolyzers. However, the study of gas-involving electrocatalytic processes is currently associated with several issues, including slow mass transport of gases to the reaction interface and lack of analytical tools that facilitate the online and immediate analysis of the product distribution. Although some methods have been developed to alleviate these barriers, such as the rotating disc and rotating ring-disk electrodes (RDE and RRDE) and thin-layer flow cells,[1-2] the mass transport is still intrinsically limited by the low solubility of gases and they are also not suitable for real time and in situ characterisation of complex (gaseous) products. These limitations have adversely hindered the assessment of reaction kinetics on electrocatalysts, and the appropriate understanding of reaction mechanisms and dynamics.

In this regard, we demonstrate the use of the gas accessible membrane electrode (GAME) as a versatile tool for electrocatalysis research. The GAME system takes the benefits of the previous floating electrode technique,[3] allowing low-loading (μg cm^{-2} scale) catalysts to be deposited. By employing an efficient gas-circulating loop, the GAME enables the gaseous reactants to be directly utilised from the gas phase, leading to higher current densities (~ hundreds of mA cm^{-2}) than conventional configurations. Moreover, the GAME can be merged with other techniques, such as mass spectroscopy and Fourier-transform infrared spectroscopy (FTIR), evolving into a series of correlative platforms for evaluating the products that are simultaneously collected from the reaction interface. As shown in Figure 1, these correlative platforms have a myriad of applications, and in situ/operando characterisation of reaction products can be carried out with high temporal resolution, providing mechanistic information about reactions involving multiple pathways (i.e. CO_2 reduction).[4] This work contributes to high-throughput screening of electrocatalysts and further offers promising strategies for the rational design of electrode structures and reactors for practical implementation.

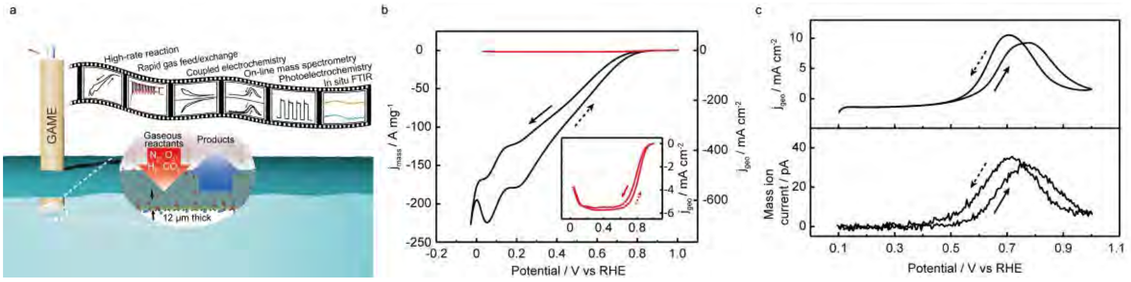

Figure 1. (a) Schematic of the GAME and possible applications. (b) Comparison of cyclic voltammograms for oxygen reduction reaction obtained from the GAME (black) and RDE (red). (c) Representative cyclic voltammogram and mass spectrometric cyclic voltammogram of CO_2 (m/z=44) for methanol oxidation.

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Crosslinked Polymer Electrolytes Encompassing Protic Ionic Liquids: A New Class of Solid Electrolytes for Energy Storage Devices

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In the last years, the use of polymer-based electrolytes in electrochemical energy storage devices has been intensively investigated due their favorable properties in terms of electrochemical/chemical stability and safety (leakage free).[1] Although most of these studies have been dedicated to the use of polymer electrolytes in batteries, they have also been used in electrochemical double layer capacitors (EDLCs), as well as with fuel cells.[2]

Polymer electrolytes encompassing room temperature ionic liquids (RTILs) show interesting features in terms of enhanced ionic conductivity, wide electrochemical stability and successful utilization in high-performance lithium-ion batteries (LIBs) and EDLCs.[3] The large majority of these studies have been conducted employing aprotic ionic liquids (AILs), which are the most commonly used RTILs for energy storage applications. Protic ionic liquids (PILs), on the other hand, have only been used in fuel cells, so far.[4]

In this work, we present for the first time a protic ionic liquid-based polymer matrix, based on n-butyl pyrrolidinium bis(trifluromethylsulfonyl)imide ($PYR_{H4}TFSI$) and soft crosslinked polyethylene oxide (PEO) that shows remarkable cycling stability as electrolyte and separator in lab-scale EDLCs as well as Li-metal cells. The innovative polymer electrolytes are produced by UV-induced polymerization, which is easily scalable, rapid, highly efficient and green.[5] Crosslinking allows the incorporation of high amount of RTIL and lithium salt, leading to polymer electrolytes with remarkable homogeneity and robustness. The thermal and transport properties, as well as the reactivity with elemental lithium of this innovative electrolyte have been investigated. Furthermore, its use in combination with activated carbons (AC) in addition to lithium iron phosphate (LFP) and lithium nickel manganese cobalt (NMC) cathodes has been studied and successfully demonstrated for the first time. The results of these studies indicate that protic ionic liquid-based polymer electrolytes can be considered as a novel and very interesting class of electrolytes for the development of safe and high performance EDLCs and even Li-metal based batteries.

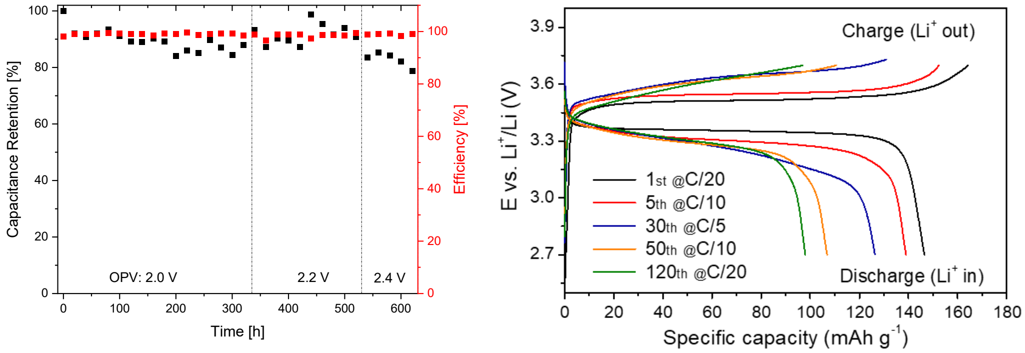

Figure 1 Stability investigations via float tests of an EDLC using the PIL based polymer electrolyte (left) as well as proof-of-concept rate tests via galvanostatic charge discharge measurements of a LFP based lithium metal polymer cell (right).

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Effect of endothelial cell networks on respiratory activity of spheroids

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Three dimensional (3D) cultured cells such as spheroids are gaining much interest in drug screening and regenerative medicine as they express relevant characteristics to *in vivo* in comparison with two-dimensional (2D) cultured cells. However, engineering of thick 3D cell constructs is a challenging issue, because cells inside a large engineered construct lack sufficient supply of nutrients and oxygen, resulting in poor cellular viability. Incorporation of vascular structures in 3D cell constructs is one of the strategies to overcome this problem, expecting the endothelial cell (EC) networks to enhance mass transportation.
To support the elaboration of engineering tissue models, evaluation system for 3D cell constructs needs to be developed. Since electrochemical measurements provide label-free in situ analysis, we have been developing various electrochemical devices including probe electrodes and on-chip devices and adapted for evaluation of 3D cell constructs [1].

In this study, we fabricated fibroblast spheroids containing EC networks for the preliminary step of vascularized tissue models. With the incorporation of EC networks, the cellular activity as well as the capacity of drug penetration may differ. As oxygen consumption is one of the fundamental cellular functions of cells, we performed electrochemical measurement of respiratory activity for the spheroids with both non-treated and drug-treated conditions [2] (Fig. 1).

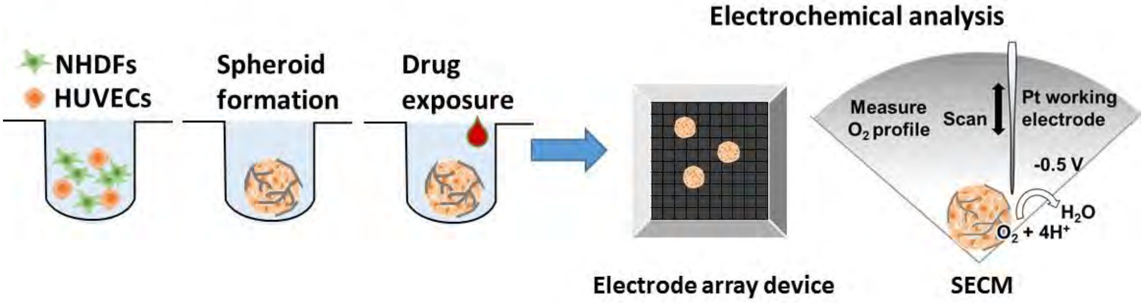

Fig. 1 Schematic illustration of electrochemical measurement of spheroids containing EC networks

For spheroid fabrication, human umbilical vein endothelial cells (HUVECs) and normal human dermal fibroblasts (NHDFs) were co-cultured at different seeding ratios (HUVEC concentrations of 0, 10, and 30%) in a hanging drop-based microwell plate. To investigate the drug sensitivity of the spheroids, doxorubicin (DOX) was added during the culture. The electrochemical measurement of respiratory activity was performed with scanning electrochemical microscopy (SECM) and an electrode array device.

During culture, HUVECs were partially connected to each other and formed networked structures. After DOX treatment, the respiratory activity of the spheroids with 10% HUVEC ratio was relatively small compared to those of 0% HUVEC, whereas, there was little difference between those in diameter. The incorporation of HUVEC networks in the spheroids promoted the penetration of DOX, resulting in lower respiratory activity in the spheroids with higher HUVEC ratio. Overall, respiratory activity may be a sensitive indicator for drug capacity of spheroids containing EC networks.

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Scanning Gel Electrochemical Microscopy (SGECM): Local Electrochemistry with Flexible Spatial Resolution

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Scanning gel electrochemical microscopy (SGECM) is a new scanning electrochemical probe technique that measures spatially localized electrochemistry based on gel probes in contact with the sample surface. So far, the gel probes are fabricated by electrodeposition of chitosan on micro-disk electrodes or etched metal wires and approached to the sample by current or shear force feedback. Proof-of-concept works have been published for topography, amperometric and potentiometric mapping [1, 2].

Like in any other scanning probe technique, spatial resolution is a key characteristic of SGECM, which determines the applications and the market. Especially considering the soft nature of gel, the contact area between the gel and the sample surface is tunable by pressing or stretching the gel. This offers an important feature of SGECM, that is, flexible resolution with the same probe, which is quantitatively analyzed from two aspects in this work: (1) marking single sampling points by locally oxidizing Ag to AgCl and measuring their size **(Figures 1 and 2)**; (2) line scan over reference samples with periodic topography and composition **(Figures 3 and 4)**. It is revealed that for an optimal gel probe based on 25 µm diameter Pt disk electrode of $R_g \approx 2$, the lateral physical resolution of SGECM at contact position is *ca.* 50 µm for current feedback and *ca.* 63 µm for shear force feedback. More importantly, it can be flexibly tuned in the range of 14 to 78 µm by pulling or pressing the gel probe after touching the sample. Current feedback is more sensitive to gel-sample contact than shear force feedback, but the latter is more versatile which is also applicable to non-conductive samples.

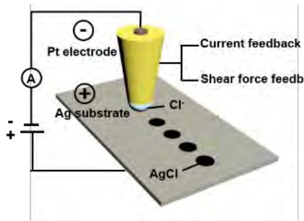

Fig.1 Scheme of SGECM patterning.

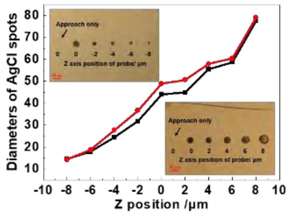

Fig.2 AgCl depositions on Ag substrate.

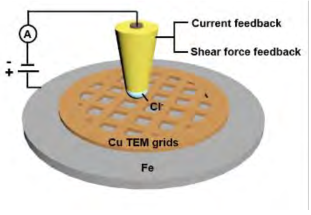

Fig.3 Scheme of SGECM line scan.

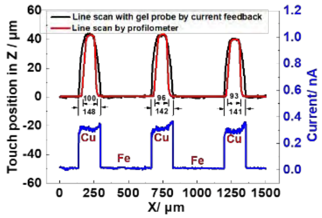

Fig.4 Line scan of profile and steady state current.

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Intelligent Microelectrodes Array for Schizophrenia Treatment Monitoring

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Schizophrenia (SCZ) is a chronic mental disorder that affects 23 million people worldwide [1]. Clozapine (CLZ) is the most effective antipsychotic medication for treatment-resistant SCZ patients. Despite the superior efficacy of CLZ, it is dramatically underutilized due to the unavailable objective tests to measure CLZ efficacy [2]. Several redox biomarkers in the blood have been correlated to CLZ efficacy. Yet, existing analytical methods change the molecules levels, their redox state, and eventually destroy the sample. By bridging the analytical gap and profiling the redox biomarkers, rapid and accurate CLZ treatment efficacy monitoring can be provided. Our overall goal is to develop a novel intelligent electrochemical biosensor based on an array of microelectrodes for CLZ treatment efficacy analysis. Here, we present the fabrication of the microelectrodes array, modification of the array with diffusion-limiting films, and characterization of the film's effect on the generated electrochemical activity. The novelty of the biosensor lies within an array of microelectrodes modified with the positively charged biopolymer chitosan generating a set of complex electrochemical signals that are analyzed by using intelligent chemometric models. To achieve our goal, we microfabricated an array of 24 gold microelectrodes (100-µm-diameter working and 1,500-µm-diameter counter electrodes) by using photolithography and thin film deposition techniques (Fig. 1A). We used a 1.2% chitosan solution and applied cathodic current to electrodeposit thin films of chitosan onto the microelectrodes. To fabricate chitosan films with similar thicknesses and different densities, we measured the relationship between the thickness of the electrodeposited film and the applied electrodeposition current for 90s and 180s durations (Fig 1B). A similar wet chitosan thickness (57.6±0.8 µm) was successfully achieved with 510 nA for 90s and 950 nA for 180s durations. Moreover, different dry chitosan thicknesses were obtained for 90s (10.7±0.1 µm) and 180s (13.2±0.6 µm) durations. Therefore, we calculated the porosity of the electrodeposited films as the ratio between the thicknesses of the wet and the dry films (5.38±0.09 and 4.36±0.20 at 510 nA for 90s and 950 nA for 180s, respectively). Furthermore, we used cyclic voltammetry to characterize the permeability of the modified films by measuring the ratio of the electrochemical signals generated from differently charged redox molecules (negatively charged ferrocyanide, neutral ferrocene, and positively charged hexaammineruthenium) before and after the modification (Table 1). Statistical T-test analysis of the resulted permeabilities revealed significant differences for the charged molecules (P=0.85% for ferrocyanide; P=4.57% for hexaammineruthenium), while no significant difference was observed for the neutral molecule ferrocene. By providing a new way to analyze molecular profiles in blood, we anticipate establishing a new detection scheme for CLZ treatment efficacy that will help to transform schizophrenia management.

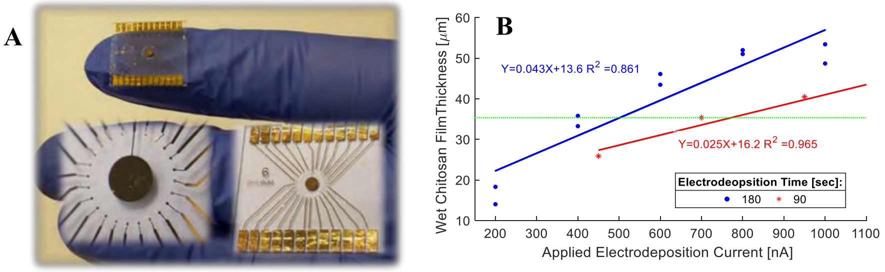

***Figure 1**: **(A)** Optical photos of the fabricated microelectrodes array. **(B)** The relationship between the wet chitosan thickness and the applied electrodeposition current for 90s (red stars) and 180s (blue circles) durations. The resulted calibration curves enabled calculating the conditions required to achieve chitosan films with similar thicknesses and different porosities (horizontal green line).*

***Table 1**: The influence of differently charged redox molecules on the permeabilities measured with the chitosan modified electrodes.*

Molecular properties		**Ferrocyanide**	**Ferrocene**	**Hexaammineruthenium**
Molecular weight / Physiological charge		211.95 / -4	216.06 / 0	197.2 / +2
Applied current	Electrodeposition duration	Modified electrode permeability for each molecule		
510 nA	90s	1.26 ± 0.02	0.757 ± 0.131	0.429 ± 0.020
950 nA	180s	0.972 ± 0.051	0.678 ± 0.056	0.379 ± 0.025

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Electrochemical Corrosion Studies on Carbon Containing CrFeNiMnCo Thin Films in Acidic Environments

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Based on the equimolar High Entropy Alloy (HEA) composition CrFeNiCoMn [1-3], multi-component thin films about 500nm in thickness were deposited by means of dc magnetron sputtering on a Si substrate. Different amounts of carbon corresponding to 0 to 10 at. % were added to the films, which simultaneously increased the film ductility and hardness as well as changed the structure of the material [4]. The films were studied regarding their electrochemical corrosion properties in acidic environments such as 0.05 M H_2SO_4 and 0.05 M HCl aqueous solutions and the results were compared with those obtained for a CrFeNiCoMn bulk sample. The results indicate improved corrosion properties of the thin films due to their more homogeneous elemental distribution. The role of the carbon in terms of corrosion was studied using SEM/EDS, XRD, XPS/HAXPES, ICP-MS and electrochemical experiments, such as cyclic voltammetry, polarization curves and impedance spectroscopy (EIS). A beneficial influence of carbon was observed below 0.8 V vs. Ag/AgCl in H_2SO_4 and at potentials above 0.8 V vs. Ag/AgCl in HCl. The latter indicates a decreased pitting corrosion tendency in the presence of carbon.

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Polyfluroalkyl substances sensing with serum proteins: transposing toxicological studies to biosensing strategies

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The study of the interactions between per- and polyfluroalkyl substances (PFAS), a class of ubiquitous global contaminants, and serum proteins can improve the design of protein-based electrochemical biosensors for the on-site monitoring of these perfluorinated compounds in natural and industrial waters [1]. In the last decade, the affinity of PFAS for serum proteins (particularly albumins and globins) was subjected to extensive toxicological studies to explain their accumulation patterns, elimination rates and toxicity [2]. To transpose these findings in the design of bioreceptors, human serum albumin (hSA) was first considered. Untreated and delipidated hSA performances towards perfluorooctanoic acid (PFOA) binding were characterized with a multi-analytical approach. Isothermal titration calorimetry measurements allowed to define the stoichiometry and the affinity constants of the complexes showing a higher reproducibility of the binding event with the delipidated hSA. The stability of this latter was confirmed also by collision induced unfolding analysis performed by native nano-electrospray ionization mass spectrometry. Moreover, the molecular basis of PFOA interactions were clarified by the X-rays crystallography. Delipidated hSA was confirmed to be a more suitable bioreceptor than untreated hSA and so further applied in a proof-of-concept study for the development of an impedimetric biosensor. Aiming to design a portable device, the bioreceptor was immobilized at graphite screen-printed electrodes previously modified with pyrrole-2-carboxylic acid (Fig.1). This step was instrumental to obtain carboxylic acid groups on the surface to immobilize the protein via EDC/NHS coupling and to improve the conductivity of the working electrode. The impedimetric data interpretation was supported by the small-angle X-ray scattering analysis of the bioreceptor-target complex. A parallel investigation of PFAS impact on globins activity was performed following the changes in the heme electroactivity in presence of perfluorooctane sulfonic acid (PFOS) and PFOA. The results suggested the potential of serum protein-PFAS interactions monitoring for sensing, toxicological as well as precision medicine applications.

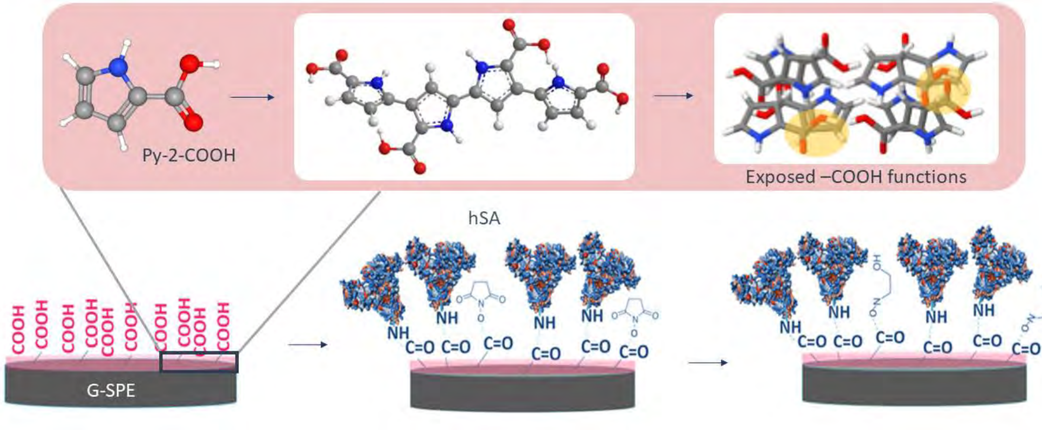

Fig. 1. Schematic illustration of the procedure optimized for human serum albumin immobilization at graphite screen-printed electrodes for the impedimetric biosensing of perfluorooctanoic acid.

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Oxygen Evolving Activity and Stability of Nanoparticulate Pyrochlores with Mixed Occupancy in B Sites

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Efficient electricity storage in chemical bonds is of vital importance for the replacement of fossil fuels with renewable energy sources. Hydrogen is a particularly suitable energy-rich molecule capable of renewable energy storage. Electrolytic hydrogen production is, however, limited by the sluggish kinetics of the electrocatalytic oxygen evolution reaction (OER) which is difficult to optimize. The state of the art OER catalysts are based on oxides of Ru and Ir the feasibility of which is compromised by the catalysts cost or stability. Hence, there is a great motivation to develop novel catalysts based on these elements which show increased stability with simultaneous reduction in the noble metal content.

This paper reports on synthesis and behavior of novel pyrochlore ($A_2B_2O_7$) catalysts simultaneously containing iridium and ruthenium in the B-site. Mixed Ru/Ir pyrochlores with a fraction of Ru in the B-site of x_{Ru} =0.2, 0.4, 0.6, 0.8 were synthesized by the spray-freeze freeze-dry approach The pyrochlores if stabilized with trivalent lanthanide in A site are single phase materials showing promising activity in oxygen evolution reaction (OER) in acid media. Increased catalytic activity of the pyrochlore based catalysts is achieved by the coexistence of Ir and Ru in the B-site of the pyrochlore structure. The observed activity is not, apparently, dependent on the size of the lanthanide (Yb, Gd, or Nd) cation in the A site and in this manner on the lattice constant of the prepared materials (see Fig. 1). All prepared mixed pyrochlore catalysts are surpassing the OER activity of the corresponding iridium and ruthenium analogs featuring no cation mixing as well as that of the benchmark IrO_2 catalyst. The synergy of Ir and Ru in the B-site of the pyrochlore structure suppresses the effect of the A-site cation radius on the OER activity. The observed OER activity scales with the Ir-Ru bond distance which represents the local structure of the prepared materials. The most active ytterbium containing catalysts also show significant stability improvement under OER operando conditions over the benchmark IrO_2.

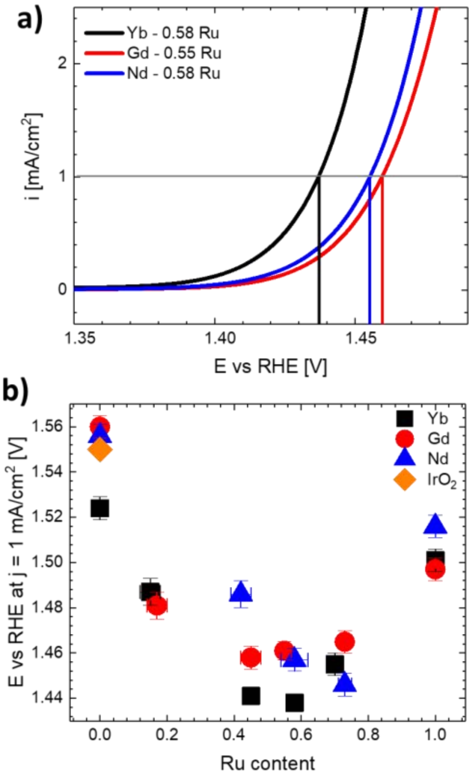

Figure 1 Typical linear sweep voltammograms of pyrochlore based catalyst samples of Ru/Ir mixed composition, measured in acidic media (0.1 M $HClO_4$, v = 10 mV/s) and b) potential in V vs RHE at a current density of 1 mA/cm² (in 0.1 M $HClO_4$) plotted versus the catalysts' ruthenium contents as determined by EDX, including the data for the pure lanthanide ruthenates and iridates.

Ageing induced exfoliation of $LaNiO_3$ perovskite OER catalysts using gelatin as a structure-directing agent

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Electrochemical production of hydrogen is a key process to chemically store the energy of intermittent renewable sources. The bottle-neck of this process is the oxygen evolution reaction at the anode, a four-electron transfer process of sluggish kinetics. Optimization of the anodic oxygen evolution is thus necessary to make this process economically feasible.[1,2] Perovskites based on first-row transition metals have been studied as cheap catalysts of abundant elements with high catalytic activity in alkaline media.[3,4]

This report outlines $LaNiO_3$ perovskites as OER catalysts that were obtained *via* spray-freeze freeze-dry synthesis with gelatin as a structure-directing agent. Using a range of different concentrations of gelatin (0.3-7.5 g/L), $LaNiO_3$ perovskite powders were successfully synthesized. Nano-particles of 30-40 nm size were obtained after calcination at 700°C in air. The morphology of the obtained nanoparticles was analyzed with both SEM and HR-TEM and shows a tendency to form distorted cubic particles as a function of the gelatin concentration used in the synthesis. The HR-TEM reveals also a large number of planar defects in the crystal growth in gelatin containing samples (Figure 1a). X-ray absorption spectra were measured for all obtained samples. The EXAFS analysis unveils Ni-rich inclusions in the structure as a result of the gelatin-based synthesis (Figure 1b).

The electrochemical activity in oxygen evolution initially shows no dependence on the gelatin concentration in the synthesis. After ageing of the electrochemical ink, a dramatic increase in OER activity is observed for the nanoparticles synthesized with gelatin concentrations of 1.5 g/L and higher (Figure 1c). This can be rationalized as an acid-induced exfoliation process along the defects of crystallographic mismatch. In return, a more active surface area is formed exposing the Ni-rich inclusions.

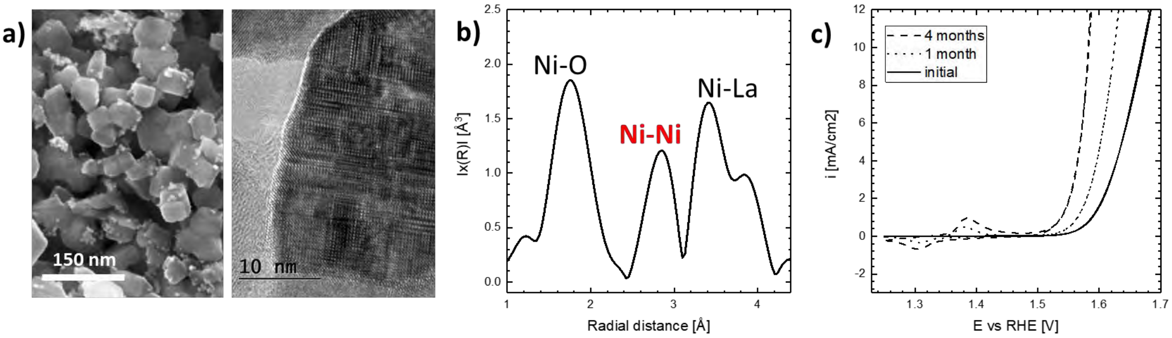

Figure 1a) SEM and HR-TEM micrographs **b)** Fourier transformed EXAFS functions measured at the Ni K-edge in R-space, weighed with k^2 **c)** cyclic voltammograms showing the OER activity of electrochemical inks initially and after ageing, all data are presented for the $LaNiO_3$ sample with 7.5 g/L gelatin concentration.

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Analysis of quasi-reversible CVs and DEIS data: transformation to potential-program independent forms

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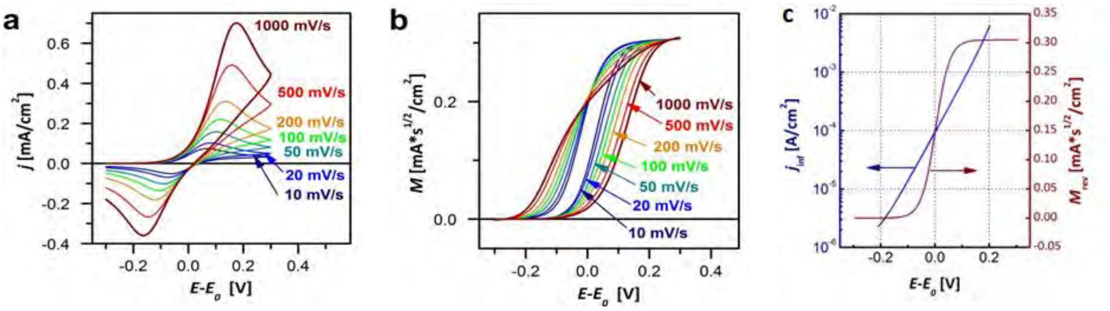
Recently a numerical procedure has been suggested by which the $j(E)$ cyclic voltammograms, CVs, pertinent to partially diffusion controlled charge transfer reactions can be analyzed [1]. Using this procedure, from a set of "quasi-reversible" CVs taken at varied scan-rates v, two scan-rate independent, hysteresis-free functions can be calculated. One of them is the diffusion-free polarization curve, $j_{\mathrm{inf}}(E)$, the other is the semiintegrated form of the reversible CV, $M_{\mathrm{rev}}(E)$.

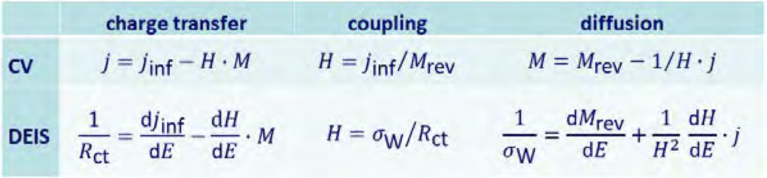
As this has been discussed in Ref. 2, the resulting $j(E) = j_{\mathrm{inf}}(E) - [j_{\mathrm{inf}}(E) / M_{\mathrm{rev}}(E)] \times M(E)$ equation is a general and exact solution to the problem of charge transfer coupled with semiinfinite diffusion. Various cases have been illustrated by numerical simulations; one is shown below.



Simulated CVs (a), their semiintegrals (b), and the calculated j_{inf} and M_{rev} functions (c). Simulation parameters: $D_{\mathrm{red}} = D_{\mathrm{ox}} = 10^{-5}$ cm²/s, $c_{\mathrm{red}} = 10^{-6}$ mol/cm³, $c_{\mathrm{ox}} = 0$ mol/cm³, $E_0 = 0$, $k_0 = 0.001$ cm/s, $\alpha = 0.5$.

Separating the contributions of charge transfer and diffusion to electrode kinetics can be done also by measuring and analyzing electrochemical impedance spectra (EIS). Parameters characterizing charge transfer and diffusion are R_{ct}, the charge transfer resistance and σ_{W}, the Warburg coefficient. These can be calculated from impedance spectra measured under *dc* conditions and also from spectra recorded during potential scans. This latter method, the combination of (sufficiently low scan-rate) CV and (sufficiently high frequency) EIS is called dynamic EIS (DEIS).

Both R_{ct} and σ_{W}, obtained from DEIS, depend on the scan-rate. However, the scan-rate dependence can be eliminated using the linear equations derived in [3]. As a result, we have the following set of equations connecting the measured j, M, R_{ct} and σ_{W}; the coupling parameter H $(= k_{\mathrm{ox}}/\sqrt{D_{\mathrm{red}}} + k_{\mathrm{red}}/\sqrt{D_{\mathrm{ox}}})$ is composed of rate and diffusion coefficients only. Note the simplicity and symmetry of the equations.



	charge transfer	coupling	diffusion
CV	$j = j_{\mathrm{inf}} - H \cdot M$	$H = j_{\mathrm{inf}}/M_{\mathrm{rev}}$	$M = M_{\mathrm{rev}} - 1/H \cdot j$
DEIS	$\frac{1}{R_{\mathrm{ct}}} = \frac{\mathrm{d}j_{\mathrm{inf}}}{\mathrm{d}E} - \frac{\mathrm{d}H}{\mathrm{d}E} \cdot M$	$H = \sigma_{\mathrm{W}}/R_{\mathrm{ct}}$	$\frac{1}{\sigma_{\mathrm{W}}} = \frac{\mathrm{d}M_{\mathrm{rev}}}{\mathrm{d}E} + \frac{1}{H^2}\frac{\mathrm{d}H}{\mathrm{d}E} \cdot j$

The theory opens a new route for the high-accuracy, fast determination of charge transfer rate coefficients of quasi-reversible redox systems by employing DEIS.

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Effects of relative humidity at dry periods of wet and dry corrosion on hydrogen permeation behavior of steels

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High strength steels are widely used in automobiles, trains and construction industry with the recent demands for increase in fuel efficiency and save natural resources [1-3]. It is, however, well known that increasing the strength of steels leads to increase susceptibility to hydrogen embrittlement. To reduce the susceptibility to hydrogen embrittlement of these steels is an important issue to ensure reliability in practical use of the steels. Therefore, the deleterious effects of hydrogen on high strength steels have attracted much attention recently[4-8].

Atmospheric corrosion plays an important role in the hydrogen generation for the practical use of steels and coated steels. Some studies have focused on the hydrogen generated by atmospheric corrosion inducing the hydrogen embrittlement of steels. There are reports that the permeation rate during a wet and dry corrosion cycle showed a maximum during the drying process[9], and temperature, relative humidity (RH) and amount of sea salt on the steel surface strongly affected hydrogen entry[10]. It is not fully elucidated relative humidity on the hydrogen permeation behavior during wet and dry cycle corrosion. The purpose of this study is to investigate the effects of different RH at dry period on hydrogen permeation behavior of steels during wet and dry corrosion cycles.

The steel sheets (20 mm × 15 mm × 1 mm) were used as specimens. Both sides of the specimen were mechanically polished with SiC papers up to 1200 grit under running water. One side of the sample used as hydrogen detection side was electroplated by Ni. Before the wet/dry corrosion cycles, sample was cleaned with purified water and ethanol. The hydrogen detection side was placed on the hydrogen detection cell with 1 kmol m^{-3} NaOH solution, and the cell was placed in a RH and temperature controlled chamber. The specimens were polarized at -30 mV vs Pt during the tests. After the current of the hydrogen detection cell reached lower than 40 nA cm^{-2}, 10 μL of 0.1 kmol m^{-3} NaCl solution was placed on the sample surface of hydrogen entry side. Wet (303K, 90 %RH) and dry (323 K) cycle corrosion tests were carried out in a chamber. The RH of dry period was controlled between 65 % and 20 %. Total 12 wet and dry cycles were carried out. The temperature dependent current was subtracted from the currents that were obtained during wet and dry corrosion tests. An optical microscope and SEM-EDS were used to observe the sample surface.

The amount of permeated hydrogen through the steel during the wet/dry corrosion tests decreased with the increase of the cycle number and the decrease of the RH at dry period. Fig. 1 shows hydrogen permeation current at 4th cycle. The hydrogen permeation current during dry period decreases with decreasing RH at drying period. A relatively larger permeation current was detected when the RH was controlled at 60 % and 65 %.

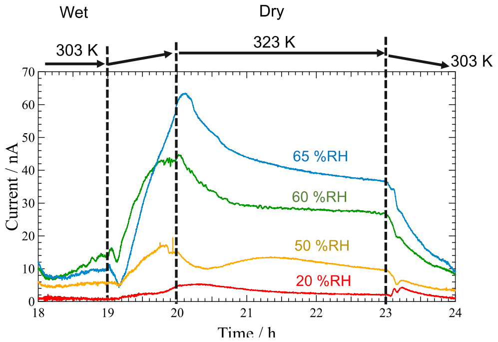

Fig. 1 Hydrogen permeation current at 4th cycle.

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Optimizing the Oxygen Electro-Reduction Activity of Pt-based Catalysts

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One of the key factors limiting the widespread applications of fuel cell technologies is the cost of the electrocatalysts utilized in catalyzing the oxygen reduction reaction (ORR) at the cathode side. More specifically, only platinum based electrocatalysts have shown sufficient activity; however, due to the scarcity and cost of Pt, it is of a particular interest to increase their activity per mass. We tackle these challenge by optimizing the size,[1] shape[2] and composition[3,4] of Pt-based nanoparticles.

Results from Pt model catalyst surfaces have demonstrated that surface defects, in particular surface concavities, can improve the ORR kinetics. It is, however, a challenging task to synthesize nanostructured catalysts with such defective surfaces. Hence, we produced Pt/C catalyst with high density of surface concavities, which was confirmed by high-resolution transmission electron microscopy, 3D-tomography, high energy X-ray measurements and positron annihilation spectroscopy (**Figure 1**). The ORR activity of the developed catalyst exceeds that of commercial Pt/C catalyst, at least 2.7-times in terms of specific (~1.62 mA/cm^2 at 0.9V) and at least 1.7-times in terms of mass activity (~712 mA/mg$_{Pt}$), which can be correlated to the enhanced amount of surface defects.[2] In a separate study, we investigated the influence of the nanoparticle size on the ORR activity. ~1 nm sized Pt nanoparticles were produced by metal organic framework template approach. The produced electrocatalyst showed mass activity of 0.87 A/mg$_{Pt}$, which was in well agreement with computationally predicted values[1] (0.99 A/mg$_{Pt}$) (**Figure 2**). Furthermore, the alloyed Pt$_x$Pr nanoparticles were synthesized and their ORR activity was investigated.[3] The alloyed nanoparticles showed 4-fold enhancement in the specific activity and 1.5 times increase in mass activity in comparison to the commercial catalyst (**Figure 3**).

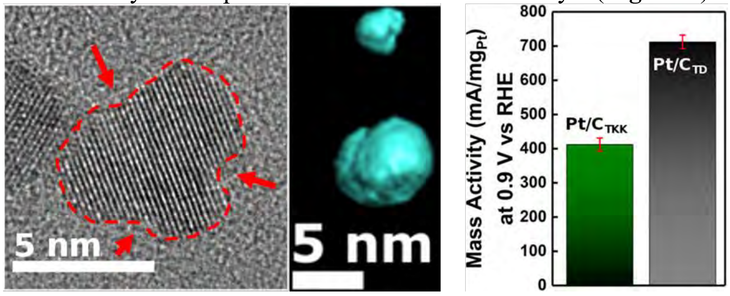

Figure 1. The ORR activity of Pt nanoparticles with high density of surface concavities. High resolution TEM and 3D Tomography images with mass activity of the Pt nanoparticles are shown in comparison to commercial Pt/C catalyst

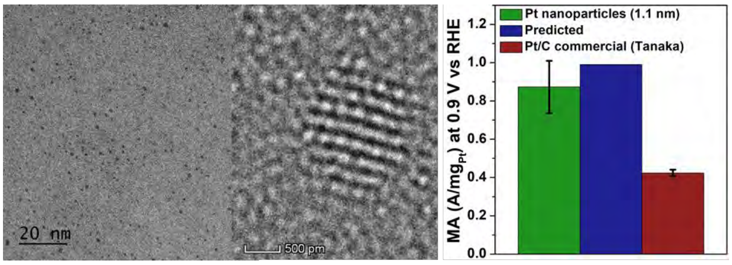

Figure 2. The ORR activity of ultra-small ~1 nm Pt nanoparticles. High resolution TEM and mass activity of the Pt nanoparticles are shown in comparison to theoretically predicted values.

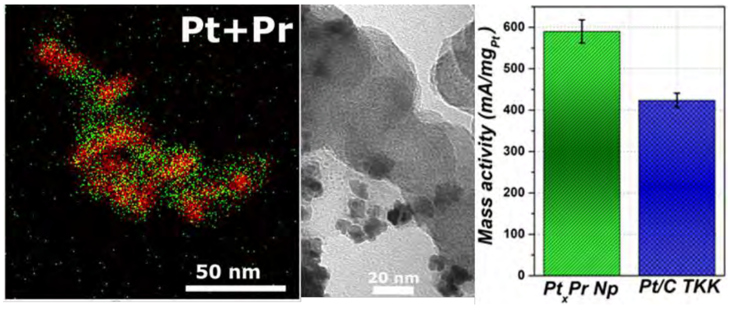

Figure 3. The ORR activity of alloyed Pt$_x$Pr nanoparticles. TEM and EDX mapping images with mass activity of the Pt$_x$Pr nanoparticles are shown in comparison to commercial Pt/C catalyst.

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Metals Dissolution in Reline and Ethaline

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Ionic liquids are inevitable solutions for the recovery of metal-based materials in future environmentally friendly and energy efficient technologies [1]. The present processes of metal recoveries are based on hydrometallurgy, pyrometallurgy and/or cyanidation, i.e. either high temperature procedures that are closely followed with high energy consumption and release of carbon dioxide, or a toxic procedure. Besides, they are associated with large amounts of wastes, in gaseous, liquid or solid form that has to go through special treatments before being disposed, which requires additional energy. Designing adequate solutions for low cost clean metal recoveries is still a great challenge. Ionic liquids are powerful solvents that could be used as electrolytes for selective metal dissolution and recovery. Deep eutectic solutions (DES) are types of low cost environmentally friendly ionic liquids that are easily prepared at large scale and with potential of being suitable for metal recoveries. They offer the avoidance of water chemistry and all the drawbacks of aqueous electrolytes. However, in order to develop the DES based metal recovery technology, the experience on metal dissolution in these electrolytes has to be gained.

To overcome these challenges, the work aims to follow dissolution of a range of metals in differently formulated DESs. Namely, the dissolution of Fe, Zn, Al and Cu will be monitored in two deep eutectic solvents: reline (choline-chloride:urea, 1:2) and ethaline (choline-chloride:ethylene glycol, 1:2). The kinetics of metal degradation in DESs will be determined by inductively coupled plasma mass spectrometry and electrochemical measurements: potentiodynamic polarization and electrochemical impedance spectroscopy. The dissolution of various metals will be followed in their natural state, i.e. at the open circuit potential, providing data about metal dissolution, for example, from the waste dust. The other way to follow the metal dissolution is by applying positive voltage to metal electrode, thus inducing electrochemical dissolution at higher rate. This technique will be assessed as a suitable one for determining better solvent for anodic leaching of metallic waste in solid form.

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Insights on the role of the copper electrode microstructure in CO_2RR

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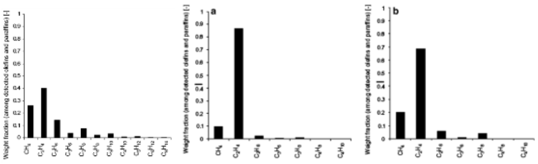
Many scientists nowadays are looking for alternative technologies to reduce the amount of CO_2 in atmosphere. Among them, one of the most promising technologies is the electrochemical conversion of CO_2 to highly-value carbon products (hydrocarbons, alcohols). This technique can be performed at atmospheric pressure and ambient temperatures. On the other hand, high overpotentials, limited stability, low selectivity and low yield are limiting the use of this technique[1].

In order to improve the CO_2 reduction reaction (CO2RR) and proceed to the upscaling on an industrial level as soon as possible, we aim to study the effect of compositional and morphological changes of copper electrodes during CO_2 reduction. We especially use copper electrodes, since they have proven to be the most efficient for the conversion of CO_2 to hydrocarbons such as methane and ethylene.

Here, we investigate the role of the manufacturing procedure of copper foils on their electrocatalytic performance for CO2RR. *Moulijn and coworkers* have previously compared the performances between Eurofysica® and Alfa Aesar® copper foils, demonstrating a clear difference in the product distribution for Eurofysica® copper electrodes before and after electropolishing procedure, in contrast with Alfa Aesar® copper electrodes that did not show any difference[2]:

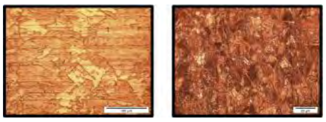


***Left image**: Eurofysica copper electrode before electropolishing, weight fraction**. Centre and right image**: Eurofysica® copper electrode after electropolishing. Product distribution after 360 min (A) and after 1160 min (B), product distribution.*

They claimed that the main parameter responsible for such difference is the difference in atoms orientation that, consequently, affects also the copper oxide amount on the copper electrode's surface, whereas the presence of impurities seems to be negligible.

Following this study, we compare commercial copper foils from multiple manufacturers, namely : Sigma Aldrich®, Alfa Aesar®, Goodfellow®, Mateck®. We link the difference in their electrocatalytic behavior for CO2RR to the surface and microstructure features:

1) Surface roughness
2) Grain sizes
3) Crystallographies and crystallite sizes
4) Different copper oxide amount



*Images after etching with HNO_3 / H_2O solution 1:1. **Left side**: Goodfellow® low purity. Variable grain size (20-50 µm). **Right side**: Eurofysica®. Average grain size: 10 µm. Magnification: 50 X.*

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Nucleation and Growth of Lithiation Patterns on Methylated Amorphous Silicon Layers Monitored by Operando Optical Microscopy

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Silicon is an excellent candidate for negative electrode materials in Li-ion batteries because of its high theoretical capacity. However, it suffers from poorly resisting to charge/discharge cycles, due to the large volume variations associated with them. We have shown that amorphous methylated silicon a-Si$_{1-x}$(CH$_3$)$_x$:H has a better cyclability than amorphous silicon a-Si:H while keeping a very large capacity [1]. This was attributed to a lower density and stiffness of a-Si$_{1-x}$(CH$_3$)$_x$:H as compared to a-Si:H, allowing for better accommodating of the volume deformation upon Li loading/release. The presence of voids in the bulk material was observed by TEM imaging and the material mechanical stiffness was measured by AFM. The chemical changes during the first lithiation was investigated by Attenuated-Total-Reflection FTIR Spectroscopy (ATR-FTIR). For a-Si$_{1-x}$(CH$_3$)$_x$:H and a-Si:H, our results indicate a two-step process in which i) a heavily lithiated phase of constant composition progressively invades the materials and ii) after total invasion, the whole electrode is progressively enriched in Li [2].

Operando observations by optical microscopy were performed on thin layers (100 nm) during the first lithiation. Unlike a-Si:H, a-Si$_{1-x}$(CH$_3$)$_x$:H undergoes a first spatially non-homogeneous lithiation [3]: lithiated zones appear on the surface as colored spots (Fig.1), which grow circularly and progressively invade the active layer. These spots have a thickness greater than that of the initial layer, which can be estimated from their color change. The morphology of the lithiation spots and their evolution are accurately determined by ex situ AFM. The resistive character of the layer is responsible for this inhomogeneous behavior. A simple model has been worked out and is in semi-quantitative agreement with the combined electrochemical and microscopy measurements.

Using Raman spectroscopy, we investigated the properties of fully lithiated, semi-lithiated and non-lithiated layers, in and out of the lithiated areas (Fig.2). Our results give some insight into the structural and electrochemical changes during the first cycle. The Li-rich layer invading the material is "opaque", i.e., optically absorbing over a large wavelength range. After delithiation, the Raman peaks are better recovered in a-Si$_{1-x}$(CH$_3$)$_x$:H than in a-Si:H.

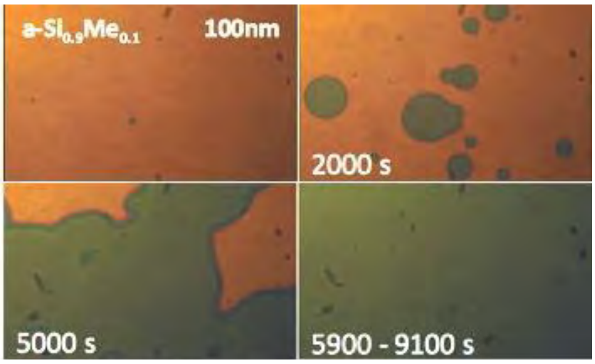

Fig.1 Non-uniform lithiation of a-Si$_{0.9}$(CH$_3$)$_{0.1}$:H

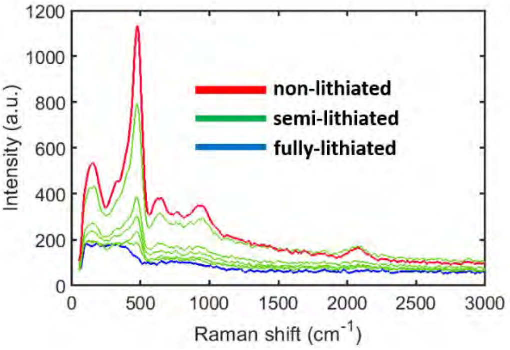

Fig.2 Raman analysis during the first lithiation

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New evidence on oxide-oxide galvanic displacement reactions

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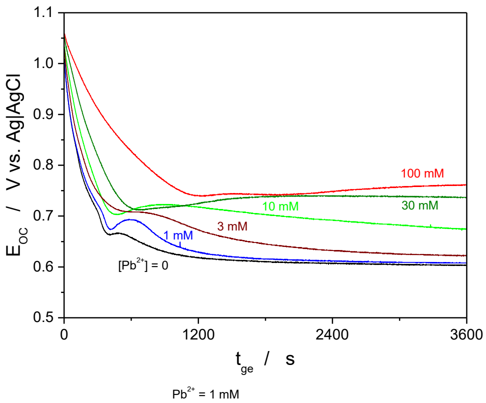
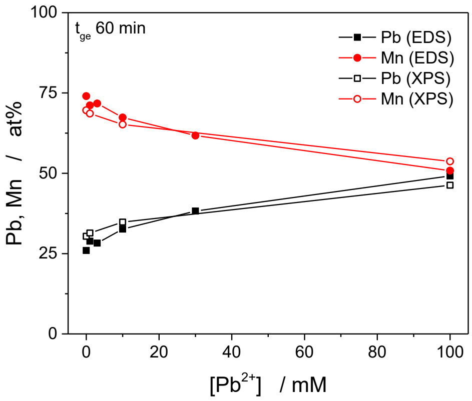
Galvanic displacement reactions between sacrificial oxides and metal cations have been used to produce secondary oxide nanoparticles [1, 2] and electrocatalytic layers [3]. Our group has investigated the mechanism of oxide-oxide galvanic displacement reactions, using PbO_2 layers and various cations (Mn^{2+}, Co^{2+}, Ni^{2+}, Sn^{2+}), reaching the following conclusions [4]: (i) There is no correlation between the thermodynamic driving force of the reaction and the secondary oxide growth rate which is controlled by solid-state diffusion of Pb species across secondary oxides. (ii) The growth occurs at the secondary oxide/solution interface; cations in solution need not to reach the sacrificial oxide to react with it. (iii) Secondary oxides contain significant amounts of the sacrificial oxide metal, i.e. they are mixed oxides.
We have collected new evidence about the effect of the concentration of Pb^{2+} ions in the solutions used in galvanic displacement reactions. In the figures we show data relevant to the reaction between PbO_2 (deposited on Au screen printed electrodes) and Mn^{2+} ions, performed with 0.02 M Mn^{2+} acetate solutions containing up to 0.1 M Pb^{2+}.





Chronoamperometric curves show that the open circuit potential (E_{OC}) declines progressively more slowly, and stabilizes at higher values, as $[Pb^{2+}]$ increases. Instead, in the absence of Mn^{2+} ions, the E_{OC} stabilizes soon after immersion of PbO_2 in the acetate solution and becomes lower when $[Pb^{2+}]$ increases, with a slope close to the theoretical value (29 mV per $[Pb^{2+}]$ decade).

By analyzing PbO_2/MnO_2 samples prepared with 1 h reaction time (t_{ge}), we found essentially identical compositions using EDS and XPS, whereas, for samples prepared with t_{ge} = 10 min, EDS yielded much higher Pb percentages than XPS. This shows that, using the thicker layers, EDS sampled only the secondary (mixed) oxide, which had a uniform bulk composition very close to the surface composition determined by XPS. By increasing the Pb^{2+} concentration in solution from zero to 0.1 M, the composition of the secondary mixed oxide changed approximately from $Mn_{0.75}Pb_{0.25}O_2$ to $Mn_{0.5}Pb_{0.5}O_2$. The larger Pb content in the secondary oxide explains the higher E_{OC} values observed at progressively higher $[Pb^{2+}]$. The marked influence of $[Pb^{2+}]$ on the secondary oxide composition shows that the reaction by which the Pb species leaves the oxide to enter the solution is reversible.

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Time-Resolved Investigation of Liquid CO_2 Reduction Products on Copper and Oxide-Derived Copper Electrocatalysts

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Valorization of waste gas CO_2 by means of electrochemical transformation is about to be realized in industrial plants. Yet fundamentals about the reaction are not understood to date. Landmark work from Hori and coworkers found that copper shows the unique capability to catalyze the formation of hydrocarbons such as methane or ethylene at high rates from CO_2.[1, 2] Later, more products of the electrochemical reduction of CO_2 such as alcohols, and aldehydes were identified.[3] Especially products containing two or three carbon atoms are interesting for a wide range of applications as fuels. Li and Kanan had success in finding a catalyst based on thermally annealed copper metal that promotes the C-C bond formation.[4, 5] Such oxide-derived catalysts show exceptionally low overpotential and high yield of liquid fuel. The product yield of such electrodes is typically quantified by established techniques such as gas chromatography, liquid chromatography, or nuclear magnetic resonance.[1-3, 6-8] Thereby, the time scale of characterization is minutes to hours. To accelerate the screening process of potential catalysts, to enable the detection of transient events and short-living products, we introduced the electrochemical real-time mass spectrometry (EC-RTMS).[9]

Herein, we present an unprecedented approach to quantify the liquid reaction products from carbon dioxide electroreduction short time after their formation on the electrode. By coupling mass spectrometry successfully to an electrochemical flow cell, we monitor seven different liquid products. By employing soft ionization, fragmentation of the compounds is suppressed. The partial currents of formation, and Faradaic efficiencies are resolved in one single potential sweep. Polycrystalline and oxide-derived copper catalysts are characterized and the role of reaction intermediates is discussed.

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Decoration Of Soft Polarized Junction With Nylon-6,6

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Under certain conditions, the liquid – liquid interface (LLI, e.g. water solution of the inorganic salt contacted to an organic and immiscible with water solution of hydrophobic salt) can be polarized and studied with the full scope of techniques offered by the electrochemical toolbox. Especially interesting are the systems where the polarized LLI is modified with functional materials. This can be achieved by means of (i) self-assembling molecules, micro- or nano-objects; (ii) polymeric or (iii) inorganic films or (iv) patterned membranes.[1] In either case the modifier brings new properties to the interfacial region that can be further harvested for sensing, energy conversion, catalysis, bio-interface development, molecular separation among many other examples.

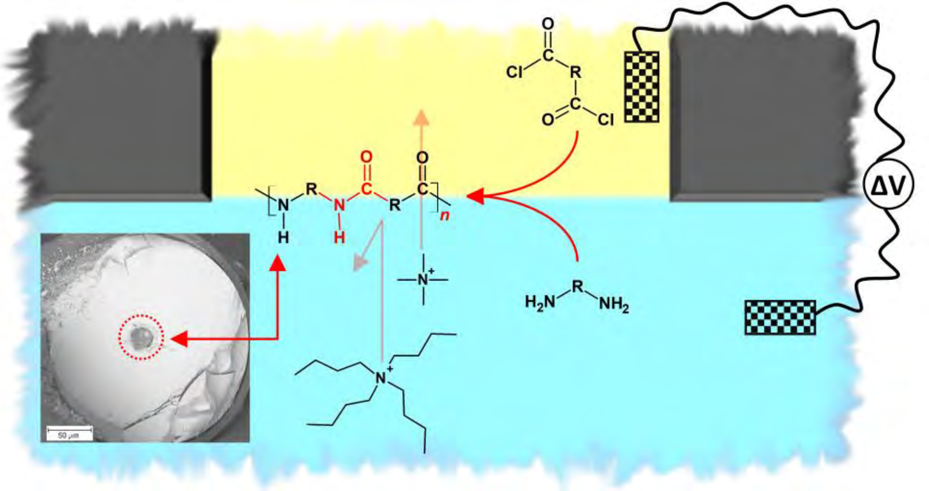

Figure 1. Schematic representation of the microscopic liquid – liquid interface modified with the nylon-6,6 and its size sieving properties.

In this work the interfacial polycondensation of polyamide (nylon-6,6,) was studied at the interface between two immiscible electrolyte solutions. The reaction between 1,6-diaminohexane initially dissolved in the water phase and adipoyl chloride dissolved in the organic phase was controlled and investigated in the presence of the potential difference applied to the soft junction from the external power source. The effect of a number of experimental conditions, this is (i) the concertation of the 1,6-diaminohexane; (ii) the concertation of adipoyl chloride and (iii) the pH of the aqueous phase on the electrochemical response of the system was studied. Optimized system was then applied for the miniaturized LLI modification (see Fig. 1). Fused silica capillaries having 25 µm in diameter were used in this respect.[2] Obtained films were then characterized with the ion transfer voltammetry showing partial and completer blockage of tetramethylammonium and teterabutylammonium cations interfacial ion transfer, respectively.

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Low-cost Fabrication of Miniaturized Platforms for Sensing at The Electrified Liquid – Liquid Interface

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Electrified soft interphases, especially the interface between two immiscible electrolyte solutions - ITIES, hold a special place in electroanalysis. This is due to a unique detection mechanism that can arise from the ion(s) crossing the liquid – liquid interface. This means that the reactions occurring at the ITIES are not limited to an electron transfer reaction. The second point that is setting the ITIES apart is the detection selectivity which is governed by the molecular partitioning between two adjacent phases, or in other words, the analyte hydrophilicity/hydrophobicity. Since the liquid – liquid interface is flowing in nature it requires a support that can be used to control its geometrical dimensions. Microscopic apertures used as the ITIES supports are especially exciting in this respect, as these can be used to improve analytical performance of the concerned platforms: (i) smaller capacitive currents lower the limits of detection, (ii) ITIES gains mechanical stability and (iii) unique diffusion layer profiles established above the soft junction assures higher mass transfer which in turn improves detection sensitivity.[1]

In this work, a few of low cost and easy to prepare electrified liquid – liquid interface (LLI) supports fabrication protocols that are applied in electroanalysis will be presented. on the focus will be given to three platforms, that are based on: (i) fused silica capillaries with a pore diameter equal to 5, 10 or 25 µm;[2,3] (ii) array of apertures with micrometer dimensions that are micro-punched in an adhesive polyamide films and (iii) 3D printed supports with complex and pre-defined geometry. These platforms are comprehensively studied and described with the help of electrochemical (e.g. ion transfer voltammetry) and microscopy (optical and scanning electron microcopy) investigation techniques. The fully operational ITIES supports are then used to study the chemical species such as illicit drugs or antibiotics (e.g. detection of cocaine in street samples,[4] ephedrine in urine or pharmacochemical study of fluoroquinolones antibiotics[2,3]). In all cases, the effect of matrix and interfering chemical species (especially cocaine street samples adulterating additives) is comprehensively described.

Acknowledgements: This project was financially supported by the **National Science Center (NCN)** in Krakow, Poland (**Grant no. UMO-2018/31/D/ST4/03259**).

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Electrochemical properties of AuNP-TiND nanostructures as glucose sensing materials and thorough interference study

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Non-enzymatic glucose sensors are prominent alternatives to the commercially available glucometers. Their main advantages over enzyme–based devices are higher stability to changes of the environment such as pH and temperature and lack of complicated immobilization procedure [1]. However, non-enzymatic glucose sensitive materials are typically less selective, so there is a strong requirement for the development of proper coatings or membranes in order to minimize the negative influence of interferences. Therefore we present Au-Ti heterostructure covered with various coatings (e.g. Nafion, poly(sulfobetaine methacrylate)) and novel approach for analysis of interfering species influence onto electrode performance in neutral solution.

Fabrication procedure of material consists of the following steps: preparing structured titanium template (TiND) by anodization and etching of nanotubes, gold sputtering and subsequent dewetting. After those steps electrode morphology is investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) [2] revealing the presence of gold nanoparticles (AuNPs) in every dimple of Ti foil. Lastly, as formed material is covered by protective coating. Electrochemical properties and catalytic activity towards glucose oxidation are determined by standard techniques - cyclic voltammetry (CV) and impedance spectroscopy (EIS). Examining interference phenomena of various compounds (such as ascorbic acid (AA), acetaminophen (AAp), urea and glycine) is realized by both CV and EIS techniques in certain configuration. Moreover, the influence of those species on the catalytic activity of the material is established. Obtained results confirm the high application potential of prepared electrodes for sensors towards noninvasive glucose detection in human body fluids.

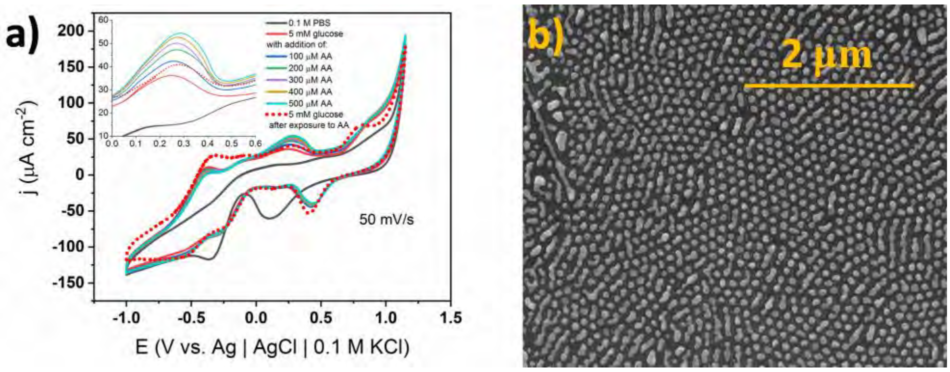

Fig. 1 a) Voltammograms of AuNP-TiND electrodes covered with Nafion in electrolyte containing different concentration of AA, 5 mM glucose in 0.1 M PBS; b) SEM image of AuNP-TiND surface.

Acknowledgements
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Scanning electrochemical microscopy at battery electrodes intermittent to charging-discharging steps at realistic current densities

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The formation of a solid electrolyte interphase (SEI) on negative electrodes is a key requirement for the long-term durability and safety of Li-ion and Li metal batteries. The chemical composition of the SEI has been analyzed by several *ex-situ* techniques [1,2]. However, the complicated composition of the SEI may be altered during sample transfer procedures (rinsing, exposure to vacuum, mechanical changes due to bending or touching the delicate layer, unavoidable contact to even trace amounts of H_2O, CO_2 etc.) [3,4]. Therefore, *in-situ* electrochemical techniques such as electrochemical impedance spectroscopy (EIS) have widely been used to diagnose the development of interphases in battery cells [5]. Those techniques provide signals that are integrated over the entire electrode surface. Among a variety of scanning probe techniques, scanning electrochemical microscopy (SECM) has been applied to probe the *local* protective properties of the SEI against electron transfers from the negative electrode to electrolyte components [6,7]. However, these studies have been conducted either in a *post mortem* scheme or under current densities much lower than used in real cells. This allows for instance the observation of incipient formation of SEI on silicon electrodes [8].

Here we propose a new cell design for SECM cell in a thin layer configuration that allows charging and discharging of battery electrodes under realistic current densities immediately followed by SECM imaging or approach curves without manipulation of the sample under study nor the electrolyte used. Finite element simulation of the secondary current density distribution proved that the current distribution deviates only slightly in the area of the opening provided that the SECM microelectrode is retracted during the charging-discharging cycles.

As an example, lithium metal electrodes were cycled in 1 M $LiClO_4$ in propylene carbonate with different current densities. The local protecting properties of the solid electrolyte interphase (SEI) were probed by SECM in the feedback mode directly within the cell in between charging-discharging cycles. The development of lithium deposits was observed by SECM and can be linked to the used charging-discharging protocol. At higher current densities protruding Li deposits are formed. Approach curves prove that the Li metal of protruding deposits is significantly more active for electron transfer to the mediator than the remaining parts of the surface. The developed hardware and methodology can be directly applied to other electrolytes or other battery electrodes forming protective films.

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The effect of naphthalene derivatives and ENSA on tin electrodeposition on gold

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Tin electrodeposition is a common electroplating process used in multiple applications: corrosion protection, electronics fabrication, packaging industry, and many others[1]; the process requires the addition of different compounds in order to have the desired chemical and physical properties of the deposit. Aromatic compounds are broadly used in tin electrodeposition and an extensive effort to understand their role during the initial stages and in the overall process has been done[2, 3]. Nonetheless, the chemical structure of the common additives is quite diverse and complex, which makes their understanding difficult.

In this work, we study the adsorption behavior of naphthalene derivatives: naphthalene (NPT), naphthalenesulfonate (NPTS) and hydroxynaphthalenesulfonate (HNPTS) on gold electrodes and their effect on the tin electrodeposition process, by means of in situ and ex situ surface analysis techniques. Experiments shown tin electrodeposition is strongly affected by the presence of NPT, NPTS and HNPTS films; tin bulk electrodeposition is inhibited in the presence of NPT and NPTS, but promoted in the presence of HNPTS. The tin deposit morphology is also remarkably modified by the presence of naphthalene derivatives. Tin deposits grown in the presence of NPT and NPTS seem to have the same morphology, but tin deposit grown in the presence of HNPTS exhibits markedly different features. Chemical composition studies revealed sulfur is incorporated in the deposit as a result of the reductive desulphonation of NPTS and HNPTS on the gold electrode.

Finally, the effect of ethoxlylatenapthalenesulfonic acid (ENSA), a commonly used additive in the tin electroplating industry, was studied on tin electrodeposition process. In good agreement with what has been shown, ENSA exhibited a similar behavior to NPT, NPTS and HNPTS during the tin deposition process in terms of the voltammetry. Nonetheless, SEM imaging shows that ENSA severely inhibits the tin bulk deposition.

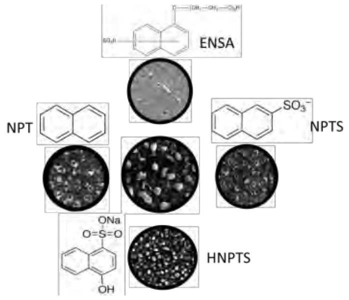

Figure 1. SEM micrographs of tin deposits morphology in the absence (center) and the presence of ENSA, NPT, NPTS and HNPTS.

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Clarifying the Working Mechanism of Mg^{2+} Complexing Agents as Electrolyte Additives for Aqueous Mg-Air Battery

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Aqueous primary Mg-air batteries have attracted much attention as promising alternative energy storage and conversion devices thanks to their high theoretical energy density, long shelf life and safety. Mg is a promising anode material. However, several drawbacks lower practical discharge potential and utilization efficiency of Mg anode. Low practical discharge potential is caused by the formation of insoluble discharge products (MgO and $Mg(OH)_2$), which reduce the active electrode surface. The low corrosion resistance of Mg anode leads to losses in utilization efficiency. One of the ways to improve the anode performance is to use the electrolyte additives that hinder formation of insoluble discharge products and keep the electrode surface clean. It has been already shown that complexing agents enhance the practical discharge performance of aqueous primary Mg-air batteries through changing the surface condition of Mg anode [1, 2]. The development of advanced Mg anode material also enhances the discharge performance of Mg-air battery. Low impurity content increase the corrosion resistance and suitable alloying elements improve the discharge activity of the Mg anodes, such as, Mg-Ca anode, Mg-Li anode, and Mg-Al anode [3-5].

In this work, we evaluate the ability of several Mg^{2+} complexing agents to improve the utilization efficiency and discharge performance by hindering the formation of insoluble discharge products and inducing uniform dissolution of Mg-Ca anode. The losses caused by chunk effect might be significant [6]. The reduction of the chunk effect by additives was also observed. The effect of the Mg^{2+} complexing agents as electrolyte additives on the discharge performance of Mg-air battery was determined via full cell discharge test. The results show that one of the Mg^{2+} complexing agents, 2,6-dihydroxybenzonate, simultaneously improves the utilization efficiency and discharge activity of Mg anode at a current density of 5 mA cm^{-2}. For a better understanding of the working mechanism of the Mg^{2+} complexing agents, the surface condition of the Mg anode in electrolyte was estimated by thermodynamic calculations to show the competition between soluble complex and insoluble $Mg(OH)_2$. Electrochemical impedance spectroscopy (EIS) measurements were performed to evaluate the surface film on Mg and to follow its evolution with time. The thickness of surface film and the resistance of discharge products were calculated based on the impedance data. Mg^{2+} complexing agents efficiently enhance the discharge performance of Mg-air battery via hindering the growth of surface film.

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Comparing doping synthesis stages of Mg-doped $LiCoO_2$ materials

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Since the commercialization of Li-ion batteries in 1991, lithium cobalt oxide ($LiCoO_2$, LCO) has been used as positive electrode material in them. Now, a few decades later, LCO is still one of the most used materials in Li-ion batteries for portable applications as it exhibits high operating potential, low self-discharge and high reversibility. As the result of three decades of investigation, several procedures to improve the performance of LCO have been proposed. These include e.g. different synthesis methods, particle morphology variation, doping and over-lithiation [1,2,3]. Several different dopants, such as Ti, Zr, Al, and Mg, have been reported to enhance the LCO performance. In addition, the synthesis methods and stages for adding the doping have been varied. However, it has not been investigated how the stage of doping affects the material properties. Therefore, in this work, the effect of the Mg addition at two different stages of synthesis on the electrochemical properties of Mg-doped LCO is investigated. In addition, the effect of Li/Co ratio of these materials on the electrochemical properties is reported as well.

The LCOs were synthesized *via* solid-state synthesis using Co_3O_4 and Li_2CO_3 as precursors. The Mg-doping was added either during the oxide precursor synthesis or during the lithiation i.e. mixing and heat-treating Co_3O_4 and Li_2CO_3. In addition, the investigated LCOs were synthesized with two different Li/Co ratios, 1.005 and 1.050.

The particle size and morphology of the LCO materials is investigated with scanning electron microscopy (SEM). Other structural characterization methods include X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The electrochemical characterization of the materials is done with galvanostatic rate capability measurements in half cells and long-term cycling in LCO/graphite pouch cells. In addition, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements are done to further investigate the electrochemical properties.

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The Importance of Nanoconfinement to Electrocatalytic Performance

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One of the main mechanisms by which enzymes achieve their high catalytic efficiency and selectivity is through the isolation of their reactive centre from the bulk solution in which the substrate is found. This results in a solution environment adjacent to the active site that is chemically different from the bulk solution. When we exploit this nanoconfinement and molecular level control in faradaic electrochemical systems, reactant species are spatially constrained resulting in high concentrations near the active electrode surface for extended periods of time. We explore how the features of the nanoconfined substrate channel that enzymes exploit (constraining the reactants, altering the solution environment and actively transporting species in the substrate channel) can be translated into electrochemical reactions to give dramatically increased reaction rates and selectivities.

Previously, we have designed a “nanozyme”, which is a nanoparticle that mimics the three-dimensional geometry of enzymes for electrocatalysis as a way to increase specific activity for the oxygen reduction reaction (ORR). This is achieved by forming isolated substrate channels that penetrate into the centre of the nanoparticle with the exterior surface electrochemically passivated by a surfactant.[1] The electrochemical reaction is then restricted to occur within a nano-confined substrate channel allowing control over the solution environment. Kinetic current density is 3.3 times higher inside the nanochannels than at the surface outside and is among the highest specific activity reported for Pt-Ni nanoparticles.

In this work, ORR activity was measured for nanozymes with different substrate channel diameters with Koutecký-Levich plots being used to calculate kinetic current density over a range of potentials in the mixed kinetic-diffusion region. Our results showed that narrow channels are more active at low overpotentials (ca. 0.95 V (RHE)), while wider channels exhibit higher activity at higher overpotentials.[2]

Physicochemical modelling of the electrocatalytic system was then employed to help explain these results. Proton and oxygen concentration profiles inside isolated channels showed that nanoconfinement is an unforeseen double-edged sword. Proton concentration is higher within narrower channels, leading to high activity at low overpotentials. This high proton concentration is not depleted as overpotential is increased, likely from proton migration into the channel due to electrical double layer overlapping. As overpotential is increased, higher oxygen depletion within the smaller channels is detrimental to activity, resulting in the larger channel nanozymes becoming more active by comparison.

Electrocatalytic nanoconfinement has the potential to greatly enhance activity by controlling reactant mass transport. This can lead to greater reaction selectivity by controlling the chemistry inside substrate channels. Greater experimental control over parameters such as channel depth and width, coupled with molecular simulation modelling, will allow us to probe this phenomenon with more detail, and hence extend this concept to other reactions where entrapment and exclusion of species in solution is vital.

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Studying fuel cell catalyst degradation in gas diffusion electrode setups

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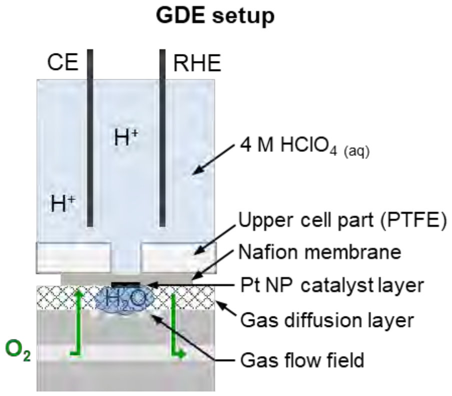

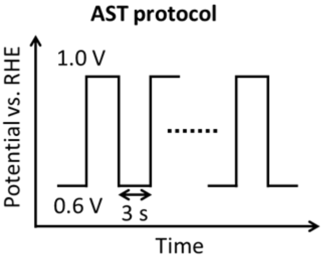

Proton exchange membrane fuel cells (PEMFCs) are a promising alternative technology for the replacement of combustion engines. The focus on the optimization of the catalyst activity in the past lead to the development of several types of highly active catalysts [1]. However, for practical applications the catalyst stability is equally important.

This work focuses on the investigation of the stability of different Pt-based catalysts to gain a better insight into the degradation mechanism of Pt nanoparticle catalysts under electrochemical conditions. [2] For this, accelerated stress tests (ASTs) are performed in a gas diffusion set-up to establishing conditions close to those in PEMFCs [3]. The applied AST protocol [4] is based on the load-cycles for an automobile proposed by the Fuel Cell Commercialization Conference of Japan (FCCJ) [5]. Applying small-angle X-ray scattering, the observed loss in active surface area upon application of the AST is correlated to different degradation mechanisms such as metal dissolution, particle detachment, Ostwald ripening or coalescence [6].

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Nanocrystalline $CuGaS_2$-based Photoelectrodes for Photoelectrocatalytic Reduction of CO_2

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The chemical recycling of CO_2 minimizes the harmful environmental effect of excess greenhouse gases in the atmosphere and can be an interesting route for renewable fuel obtaining[1]. In that sense, $CuGaS_2$-based photocatalysts were studied for CO_2 reduction under photoelectrocatalysis (PEC) technique. The $CuGaS_2$ was modified with small amounts of In or Bi to analyze the interference of these metals in the products generation. The doped and non-doped $CuGaS_2$ were deposited by spray coating on Mo using inks comprised by the respective salts of each cations, and thiourea as the source of sulfur. A CdS and TiO_2 thin films were deposited by a chemical bath deposition method on the spray-coated $CuGaS_2$ films. The photoelectrodes were characterized by XRD, Raman, SEM, EDS, Diffuse Reflectance and XPS. The photoelectrocatalytic reductions of CO_2 were performed in a one-compartment glass reactor (50 mL) equipped with quartz window, at 20 °C, with three electrodes: Pt foil as a counter electrode, Ag/AgCl (KCl sat) as reference electrode, and the semiconductors as working electrode. The working electrode was immersed in 0.1 mol L^{-1} Na_2SO_4 saturated with CO_2, irradiated by a 150 W commercial solar simulator lamp (Newport 66902) and submitted to a controlled potential (potentiostat/galvanostat - Autolab model PGSTAT 302, Metrohm) for the experiments. Aliquots of the solution were taken at controlled times and products evaluated CG-FID[2]. The photoactivity of the semiconductors were evaluated along the potential applied in the cathodic region by linear sweep photovoltammogram. Comparing the photocurrent generated for the three semiconductors, the $CuGaS_2$ and $Cu(Ga,Bi)S_2$ semiconductors presented photoactivity quite similar, while $Cu(In,Ga)S_2$ presented smaller photocurrent along the applied potentials. Once the three electrodes presented photocurrent response under the potential of -0.7 V, a chronoamperometry under transient light was performed at this potential in order to evaluate the stability of the semiconductors. The higher photocurrent is obtained with the $Cu(Ga,Bi)S_2$ electrode (0.012 mA cm^{-2}), nevertheless its photocurrent decreases around 33% after 300 s, presenting at the end a photocurrent similar to $CuGaS_2$ semiconductor. The $CuGaS_2$ and $Cu(In,Ga)S_2$ electrodes presented a more stable photocurrent along the time analyzed, indicating a better stability of the material compared to $Cu(Ga,Bi)S_2$ electrode. The CO_2 reduction was performed under -0.7 V and light incidence (one sun) with the three electrodes. Comparing the amount of methanol (the main product for all the electrodes), this was higher employing $Cu(In,Ga)S_2$ electrode than under $CuGaS_2$ and $Cu(Ga,Bi)S_2$. However, the formation of other products that require a higher number of electrons and protons (ethanol and acetone) was higher under the $CuGaS_2$ catalyst. In addition, the stability and, consequently, repeatability of the products concentration formed using $CuGaS_2$ for consecutive reactions of CO_2 reduction is better than the observed for the catalysts modified with In or Bi. In fact, the Bi presence did not improve the $CuGaS_2$ activity for CO_2 reduction. After 240 min of CO_2 reduction using $CuGaS_2$ semiconductor under -0.7 V and light incidence (one sun) were quantified 1.30 mmol L^{-1} methanol, 0.45 mmol L^{-1} ethanol and 0.25 mmol L^{-1} acetone. So, despite the improvement for methanol production obtained in the first 4h of reaction with the addition of In in the semiconductor surface, the results obtained under $CuGaS_2$ electrode without further modification showed to be superior for CO_2 reduction using PEC technique.

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Preparation of porous iron oxy-hydroxide layers via galvanic displacement reactions

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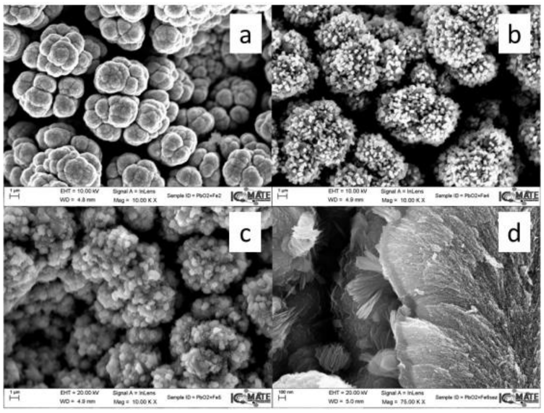
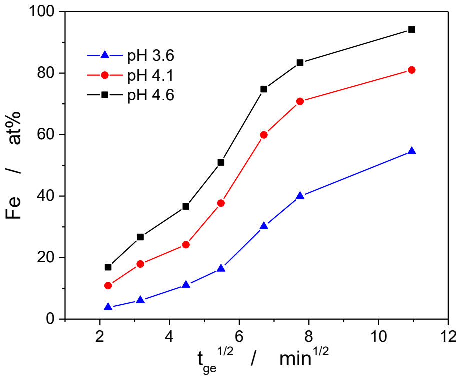
In the frame of a project aimed at the preparation of porous layers consisting of various (mixed) oxides potentially useful in electrocatalysis or energy storage, we have studied the galvanic displacement reactions between PbO_2 and Fe^{2+} ions. Following a well-established procedure developed in recent years, we have used oxygen bubble assisted anodic deposition to prepare porous PbO_2 sacrificial layers [1]. Then, we have exposed those layers to deaerated acetate buffer solutions containing 0.025 M $Fe(ClO_4)_2$, kept at 75°C, for variable reaction times (t_{ge}). The samples thus obtained have been submitted to SEM-EDS, XPS and XRD analyses, revealing a behavior significantly different from those of other previously described systems [2, 3].





SEM images recorded after different reaction times (from a to c, 10, 45 and 120 min, respectively) show distinct growth centers which progressively increase in size to completely cover the sacrificial oxide. However, the cross sectional SEM image (d) reveals that below the seemingly crystalline agglomerates, there is a continuous layer, ca. 100 nm thick, strongly adhering to PbO_2.

XPS analyses show that, at the surface of the secondary layer, iron is present as Fe(III), and that the oxygen peak is accurately fitted by two contributions with comparable intensity due to oxide and hydroxide environments, respectively. XRD analyses show the presence of crystalline γ-FeOOH (and minor amounts of α-FeOOH), in addition to the mixture of α-PbO_2 and β-PbO_2 already observed [1]. Thus, XPS and XRD data converge to suggest FeOOH to be the main component of the secondary layer, not excluding the presence of other amorphous compounds. As reported for secondary oxides of other metals [2,3], XPS reveals the presence of Pb, at variable percentage depending on the reaction duration. In the initial stages ($t_{ge} \leq 10$ min), corresponding to the formation of the continuous layer, the secondary oxide contains 5.5 at% Pb; for $t_{ge} = 1$ h, when the sample is covered by the crystalline material, the Pb content drops to 1.5 at%.

EDS analyses, as long as their sampling depth is larger than the secondary layer thickness, give qualitative information on the growth rate, although they are unable to provide the exact composition of the latter. The time dependence of Fe percentage shows that the growth rate is higher at higher pH value. It also shows different growth regimes which one might tentatively associate with the change in morphology shown in SEM images and with the variable Pb content in the secondary oxide layer.

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Testing Corrosion Stability of ZrO_2 coating on sample AA 7075

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Zirconium-based coatings are one among many attempts to replace coatings based on chromium(VI) compounds, which have been proven to cause bad effects on human's health and their surroundings, as less harmful and ecologically accepted alternatives [1,2]. On the other side, mechanisms for corrosion inhibition and suppression are subjected to myriad discussion of both academic and industrial researches. This research was carried out on an aluminum sample AA 7075 and the corrosion stability of zirconia (ZrO_2) as an inhibitor of corrosion was tested [3]. In order to prevent agglomeration of nanoparticles the stable colloidal dispersions (sols) of zirconia were used as a source for deposition of nanoparticles. Zirconia sols were synthesized by forced hydrolysis of aqueous solution of zirconium salt ($ZrOCl_2$), resulting in well dispersed particles with uniform size. Two sols were synthesized, diluted (0.4 wt.% solid phase content) and concentrated (0.8 wt.%). The particles size distribution (hydrodynamic diameters) was in the range 30-120 nm for both sols, with average particle size of about 60 nm. Zirconia nanoparticles were deposited on a metal surface by immersion in both diluted and concentrated ZrO_2 sol. Throughout the research, multiple methods were combined: scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and open circuit potential (OCP). The OCP monitoring indicated a three-step process of zirconia deposition: initial short dissolution of Zn intermetallic particles from AA 7075, followed with native oxide layer dissolution and subsequent zirconia film deposition and thickening. It was shown that the inhibition effect of zirconia coatings depends on its two general characteristics: thickness and porosity. With the information collected by scanning electron microscope, it was established that the zirconia particles coated homogeneously the underlying surface and assembled into a porous deposit. The results indicated that the zirconia layers formed from the concentrated sol had pores penetrating deeper inwards the substrate, as compared to the one deposited from the diluted sol. This was confirmed by the EIS data in 0.05 mol dm^{-3} NaCl.

The total impedance of layer obtained from dilutted sol increased with time of immersion in NaCl solution and EIS response was characterized with two time constants. The resistance of coating deposited from concentrated sol was considerably smaller than of that deposited from diluted sol. Furthermore, the coating deposited from concentrated sol resembled the AA 7075 response, while the one obtained in diluted sol offered longer protection of the aluminum substrate.

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Investigations of Reversible Voltage Losses and their Recovery after Dry Operation in PEMFCs: Some Mechanistic Insights

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Over the last years, fuel cell electric vehicles (FCEVs) have been experiencing rapid development and are regarded as promising alternatives for battery electric vehicles with regard to their long driving range and low refueling time. However, cost and durability of polymer electrolyte membrane fuel cell (PEMFC) stacks remain the main obstacle for successful commercialization of FCEVs. Over the lifetime of a PEMFC in an FCEV, certain duration of dry operation and/or dry-wet cycling is hardly preventable. It is known that significant reversible voltage losses (several hundred mV) take place under these conditions [1].

In order to keep the cell performance high and prevent reversible losses from developing into irreversible ones [2], the standard approach is to apply proper recovery steps of certain frequency. In the literature, various recovery procedures could be found, such as increasing inlet gas humidity, lowering cell potential and switching cathode gas to nitrogen [1]. There are also reports about using air as cathode gas during recoveries [3]. One other possible way of mitigating or preventing the reversible voltage losses under these conditions is to develop catalyst layers that are less prone to the degradation phenomenon. For this purpose, a detailed understanding of the degradation mechanism is essential. In the literature, the reversible losses after dry operation are explained either by adsorption of ionomer sulfonic groups to the Pt surface and poisoning of the latter [1-2,4], or by degradation of Pt/ionomer interface in the catalyst layer [1].

In this work, we tackle the problem of reversible degradation by first evaluating the effectiveness of various recovery protocols found in the literature [1,3] or designed in-house. Comparing the mass activity regain after recovery steps, we conclude that the application of diluted air might be of significant advantage by showing its superior water management and relatively low cathode potential, both known to favor recovery from dry operations [1]. We then use the found recovery protocol and investigate whether catalyst components influence the reversible losses. Hereby, we focus on the effect of carbon surface modification [5-6] and the change in ionomer content in the catalyst layer. With electrochemical characterization methods (polarization curve, mass activity measurement, CO stripping, limiting current and electrochemical impedance spectra (EIS) under H_2/air and H_2/N_2) applied at various stages of degradation and recovery, we demonstrate some additional possible mechanisms of the losses after dry operation, including ionomer reconstruction and decrease in catalyst layer proton conductivity. These findings serve as input for future operation strategies as well as catalyst layer development to reduce the adverse effects of those reversible degradations during PEMFC lifetime to a minimum.

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Thermal Investigation of Innovative Electrolytes for High Voltage Electrochemical Capacitors

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The development of innovative electrolytes is considered of key importance for the realization of Electrical Double Layer Capacitors (EDLCs) with higher energy than the state-of-the-art devices.[1-3] For this reason, several studies have been dedicated to novel solvents and conducting salts in the last years, including ionic liquids, suitable for the realization of EDLCs with operative voltages higher than 3 V. The conductivity, viscosity and electrochemical stability of these electrolytes have been investigated in detail.[1, 4-6] On the other hand, only few studies addressed the thermal stability of these electrolytic solutions. These kinds of studies, however, appear of importance to understand the temperature range of use of the devices.

In this study, we are reporting a detailed investigation on the thermal stability of four electrolytes based on the solvents propylene carbonate (PC), adiponitrile (ADN), butylene carbonate (BC), 3-cyanopropionic acid methyl ester (CPAME) and on the salt 1-butyl-1-methylpyrrolidinium tetrafluoroborate ($Pyr_{14}BF_4$). In all electrolytes, the salt concentration was set to 1 M. All these electrolytes are suitable for the realization of EDLCs with operative voltage higher than 3 V.[1, 4-5] The thermal behavior of these electrolytes during thermal ramp and isothermal experiments have been investigated. Furthermore, the effect of the confinement of these electrolytes on activated carbon has been addressed (see figure 1). Finally, the impact of the thermal stability of the electrolytes on the stability of EDLCs during float tests carried out at 60°C has been considered.

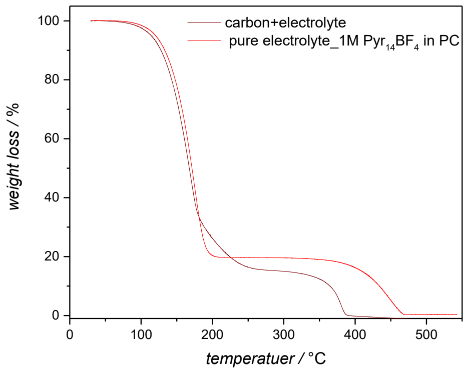

Figure 1: Thermogravimetric analysis in ramp mode of pure electrolyte (1 M $Pyr_{14}BF_4$ in PC) and carbon wetted with electrolyte. (scan rate 10°C min^{-1}).

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Investigation of the electrochemical performance of high voltage lithium-ion capacitor containing liquid and gel-polymer electrolytes

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Hybrid ion capacitors have made a tremendous impact in rising the energy density of high power energy storage devices, by integrating the battery and supercapacitor within a single device.[1-2] Amatucci et al.[3-4] first introduced the idea of combining a $Li_4Ti_5O_{12}$ (LTO) based electrode with an activated carbon (AC) based electrodes. After this pioneering work, several investigations focused on the replacement of LTO with graphite electrode, and nowadays devices based on graphite and AC are commercially available. These devices are indicated as lithium-ion capacitors (LICs) [5-6]

In this work we report an investigation about the electrochemical behavior of high voltage LICs, having an operative voltage of 4.5V, containing liquid as well as gel polymer electrolytes. We investigated the impact of the pre-lithiation of graphite electrode on the performance of these devices, and the influence of the SEI layer on their cycling stability. Furthermore, we analyzed in details the behavior of these high voltage LICs during float test at 4.5V and, also, their self-discharge. These two latter investigations, although are of high importance for high power devices, have not been systematically carried out in the past for this kind of devices, and especially for systems containing gel-polymer electrolytes. The results of these investigations are giving interesting and novel information about the operative limits of high voltage LICs and, also, about the advantages and limits related to the use of gel polymer electrolytes in these high power devices.

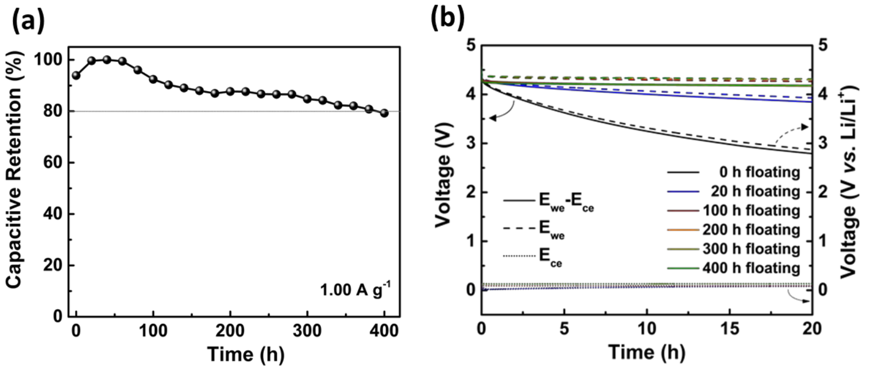

Figure 1: (a) Capacitive retention and (b) self- discharge profile of LIC at different floated hours.

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Aluminium Electrodeposition in EMImCl-AlCl$_3$ Ionogels for Improved Aluminium Batteries

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Aluminium batteries are promising candidates for the next-generation of energy storage devices, given the natural occurrence of aluminium (third most abundant element) and the intrinsic safety characteristics of the electrolytes used. The specific capacity of an aluminium negative electrode (2980 mAh g^{-1}) is comparable to that of lithium (3860 mAh g^{-1}), while its volumetric capacity of 8040 mAh cm^{-3} far exceeds that of lithium (2060 mAh cm^{-3}), due to its ability to transfer three electrons[1]. Most non-aqueous aluminium batteries utilise electrolytes including inorganic molten salts, deep eutectic solvents, organic solvents and ionic liquids, and operate by the reversible deposition/dissolution of aluminium at the negative electrode and the intercalation of the chloroaluminate ions at the positive electrode.

This work studied the electrodeposition of aluminium from the 1-ethyl-3-methyl-imidazolium tetrachloroaluminate (EMImCl-AlCl$_3$) ionic liquid and its gel form- the *ionogel*. Ionogels have previously been shown improve thermal[2] and moisture stability[3]; here, the ionogel was introduced to widen the potential stability window and enable aluminium deposition from lightweight $AlCl_4^-$ anions in Lewis neutral ionogels. Generally, aluminium is deposited by the reduction of heavy $Al_2Cl_7^-$ ions present only in Lewis acidic ionic liquids, which is generally not possible in neutral and basic compositions as the reduction of the organic cation and subsequent ionic liquid decomposition occurs at a higher potential than the reduction of $AlCl_4^-$.

Lewis acidic and neutral ionogels of varying degrees of gelation were synthesised with polyethylene oxide and EMImCl-AlCl$_3$. The electrochemical behaviour of the electrolytes was investigated by cyclic voltammetry, and aluminium deposits from the Lewis neutral ionogel were confirmed by scanning electron microscopy and energy dispersive X-ray spectroscopy. The deposition of aluminium from a Lewis neutral EMImCl-AlCl$_3$ ionogel was demonstrated for the first time (Fig. 1)[4], serving as a basis for further investigation into the role of polymer additives in developing improved ionogel and semi-solid state electrolytes for aluminium batteries.

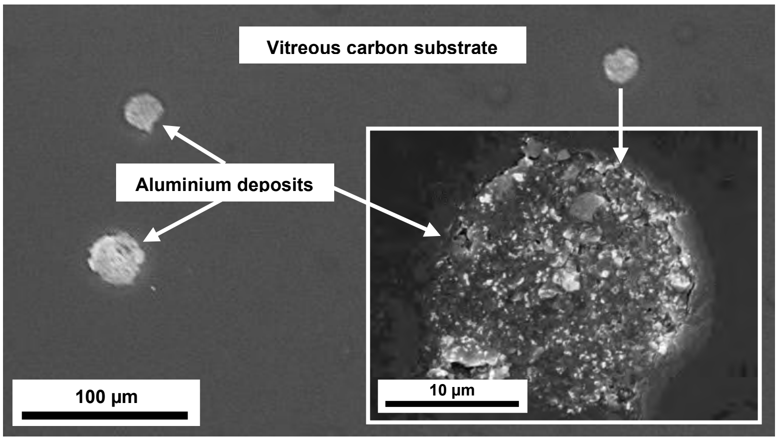

Fig. 1. Scanning electron micrographs of aluminium deposits on vitreous carbon obtained from a Lewis neutral EMImCl-AlCl$_3$ ionogel by applying a constant potential of -1.9 V *vs.* Al|Al(III) at 25ºC.

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Enhanced Cycling and Thermal Stability of Li[$Ni_{0.8}Co_{0.1}Mn_{0.1}$]O_2 Cathodes *via* Functional Organic Coatings

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The use of Ni-rich Li[$Ni_{0.8}Co_{0.1}Mn_{0.1}$]O_2 (NCM_{811}) as cathode active material is considered the next big step towards advanced lithium batteries with even greater energy density[1]. However, its wide exploration in practical applications still requires to overcome several challenges, including improvable cycling performance due to parasitic side reactions with the electrolyte, structural degradation at the particle surface, very high sensitivity towards moisture, and poor thermal stability[2,3]. The application of coatings is an effective approach to stabilize the surface of sensitive cathode material particles and to suppress detrimental side reactions at the interface with the electrolyte and/or moist air thanks to the physically prevented contact[4].

Here, we propose a novel functional organic coating which acts as protective layer to prevent the NCM_{811} from detrimental side reactions with moist air and/or the electrolyte, especially at elevated temperatures. As a result, the surface-modified NCM_{811}–based cathodes revealed enhanced cycling performance and thermal stability. Moreover, this surface coating strategy could be extended to other cathode materials, highlighting its great potential for the development of high-performance cathodes for next-generation lithium batteries.

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Selective partial covering of nanoporous gold surface with lead and evaluation of the electrochemical methanol oxidation reaction

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Nanoporous gold (NPG) has emerged as interesting material in electrochemistry due to its interesting properties, such as high surface area,[1] electrocatalytic activity,[2] tunability of surface structure,[3] among others. Previous studies have shown that NPG acts as a good electrocatalyst for methanol oxidation (MOR),[2,4] but how this reaction take place on the surface is not very well understood yet. One of the main limitations to achieve systematic studies is the necessity of a new sample for each experiment introducing variability in the surface composition and surface structure. Electrochemical studies in electrodes with a high surface area represents a challenge due to mass transport limitations in the pore space of the material and distorsion of voltammograms due to the *IR* drop. In order to overcome these limitations, a small amount of powdered NPG within a cavity microelectrode was used as working electrode.[5] This allows the preparation of multiple samples from one NPG monolith, reduces the overall current and thus the IR drop and enhances the mass transport by hemispherical diffusion to the microelectrode. By means of under-potential deposition of lead ions in alkaline media, the NPG surface was characterized. Clear signals of basal planes are obtained. The surface undergoes restructuring when it is cycled in acidic media, whereas no or less restructuring was observed in alkaline media. More interesting, controlling the bulk concentration of Pb ions, it is possible to achieve a partial coverage of the NPG surface. The energetically most favorable places are occupied first. This allows to selectively block certain sites and observe their contribution to electrocatalytic reactions such as methanol oxidation in a potentiodynamic experiments (cyclic voltammetry). This finding allowed the evaluation of the different facets of the surface towards methanol oxidation, showing that the reaction is mainly performed on the {111} terraces, contrary to the stablished notion that claim the high-energy defects are the most reactive spots. In conclusion, using cavity microelectrodes and under-potential deposition as a tool, it was possible to characterize the structure of the surface structure of internal surfaces in NPG and the reactivity of the different facets, taking advantage of the partial coverage of the surface achieved by controlling the bulk concentration of the lead.

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Hollow titania nanopillars as a flexible platform for encapsulation

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The titania nanostructures are primarily known for their potential as photoactive materials, due to their stability, corrosion resistance and flexibility of their morphologies. Their main drawback, however, is the wide electron bandgap, which greatly limits their immediate usability in the light-driven processes. Therefore, various methods of their modification have been explored, focusing on improving their overall absorption and carrier separation. For example, doping with foreign atoms [1], creating defects and vacancies [2], and introducing rib-like photonic structures [3] have all shown promise in regards to improving photoactivity of the titania nanotubes.

Today, we present an alternative method of modification of laterally spaced titania nanotubes via laser irradiation. The presented approach allows for a fast and scalable encapsulation of the nanotubes, trapping any material previously embedded within their interior. The created tightly-sealed nanostructure can be used either as a way to separate and protect sensitive material from the harsh environment, or to enhance absorption through the introduction of an extra scattering medium, like plasmonic metal nanoparticles. Moreover, the distinct separation between nanopillars, enables them to be detached from the surface independently, allowing them to be used as self-standing capsules, rather than nanopillar arrays if the application calls for it.

The newly developed hollow titania nanostructures can find success not only in conventionally research applications but also, through the versatility and biocompatibility of the titania, in biomedical applications.

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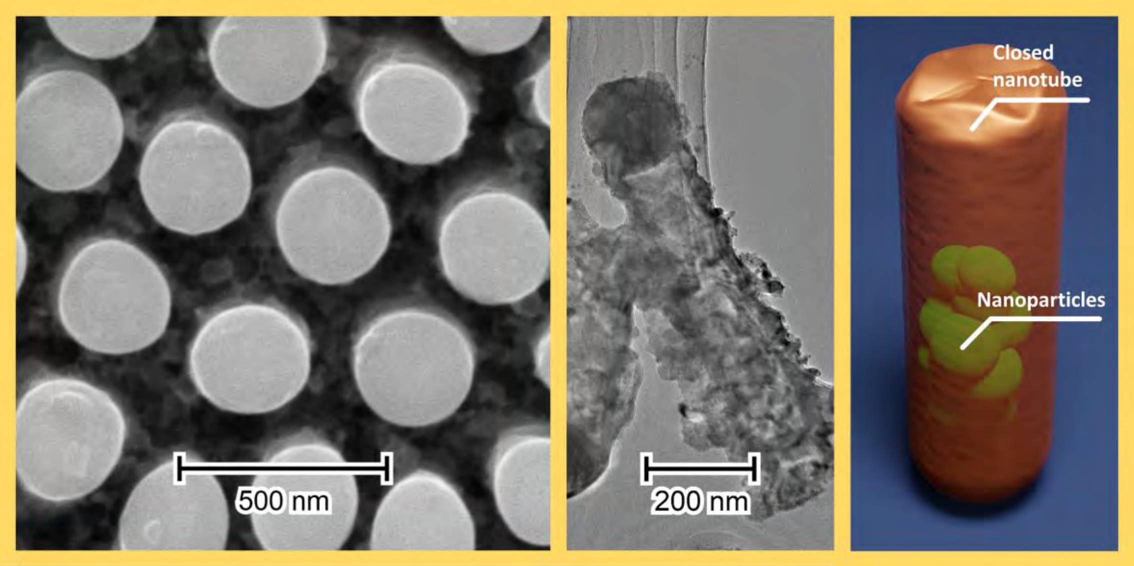

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Fast Electron Transfer Kinetics in Deep Eutectic Solvents: Effect of Water Addition

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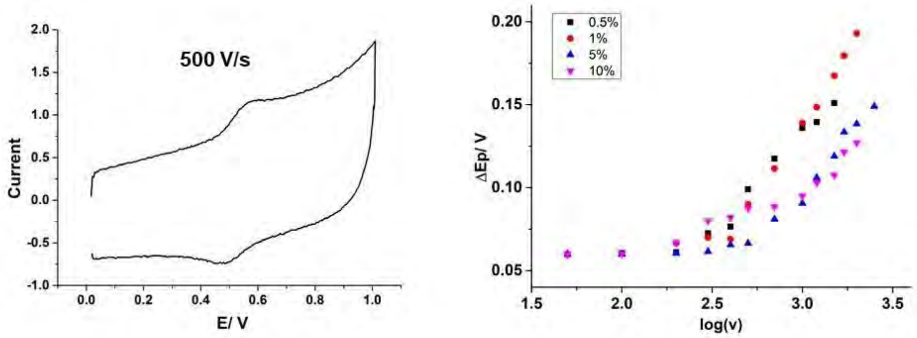
Deep eutectic solvents (DESs) are an emerging class of solvents, which is considered as sustainable and cheap alternatives to ionic liquids.(1) DESs generally consist of mixtures of salts and hydrogen bond donors producing eutectics at optimized ratio that are liquid at ambient temperature and have unusual solvent properties. Hydrogen bonding between hydrogen-donor and hydrogen-acceptor is supposed to cause the strong decrease in the melting point of the eutectics. Water amount in DESs strongly affects its physicochemical properties from density, viscosity, melting point, surface tension to conductivity,(2) while being part of DESs composition. Recent results from literature have shown that DESs' nanostructure is varied according to the amount of water present in DES.(3) It is known that DESs spontaneously absorb water when exposing in the air, to a certain extent depending on the hygroscopicity of its components. It is therefore interesting to analyze effects of water concentration on electron transfer kinetic rate constants. This point is not only a concern for fundamental molecular electrochemistry but is also meaningful for practical utility.

In a recent publication, we demonstrate that electron transfer kinetics rate constants involved in two classical oxidation reactions of ferrocene and ferrocyanide in ethaline were remarkably larger than those in ionic liquids while being comparable to values obtained in molecular solvents.(4) In this work, we will study the kinetics of oxidation of ferrocene and ferrocyanide in five DESs, including Ethaline, Reline, Glyceline, choline chloride (ChCl)-lactic acid and ChCl-malonic acid by varying the water amounts from 0.5 wt% to 10 wt% with a particular consideration of ohmic drop compensation. The extracted data in DESs shows that kinetic rate constants values considerably increase with the addition of water in DESs. Electron transfer kinetics increases much faster for the ferrocene/ferrocenium redox couple than for ferrocyanide/ferricyanide redox couple with the addition of water amount in all the five DESs.



Cyclic voltammogram and ΔEp-log(v) curve of ferrocene in Ethaline for different water additions.

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Electrodeposition of compact Ag-Ni alloys and their performances as cathode towards nitrate reduction

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Bimetallic alloys are attracting much interest for the production of efficient and cheap materials, applicable to many areas. In this context, Ag-Ni alloys are promising for applications in electric/magnetic devices and (electro)catalysis [1]. Ag and Ni have both face-centered cubic (fcc) structure, however due to large difference in atomic radii, they do not exhibit solubility at equilibrium in the solid state. Electrodeposition may generate materials of structure or composition far from thermodynamic equilibrium, made stable by their (very) slow rearrangement at room temperature [2]. However, the deposition of Ag-Ni films is complicated by a fairly large difference in standard reduction potentials, respectively 0.799 V for Ag and -0.25 V for Ni (vs NHE). Cyanide baths were used in the past to deposit Ag and Ag-based alloys, for their strong complexing action of Ag^+ ions, leading to deposition of compact films, but nowadays less dangerous solutions are preferred, both for safety and environmental concerns. Ag-Ni thin films were already electrodeposited from baths containing thiourea as complexing agent, obtaining quite compact films but also undesired sulfur inclusions up to 20% [3].

We propose here the electrodeposition of Ag-Ni alloys from concentrated chloride baths, already used in the past for deposition of Ag-Pt and Ag-Pd alloys [4]. Concentrated chloride media may dissolve various metal ions and, in the specific case, the Ag-chloride complexes $[Ag(Cl)_n]^{(1-n)-}$ are more stable than the Ni ones, bringing closer the reduction potentials and promoting co-electrodeposition.

Linear sweep voltammetries of Ag-Ni electrodeposition performed in 10 M chloride baths indicate that alloy formation occurs under transport-limited reduction of silver complexes, so that films of desired composition may be obtained by regulating the deposition current j_{dep}. The obtained films have good compactness, with globular morphology (Fig.1, left); moreover, microanalysis indicates that they are free from foreign species. XRD spectra indicate the presence of two crystalline phases, one Ag- rich and the other Ni-rich (only for Ni >50 at%) with minimal inclusions (few atoms %) of the minority species. Tests of nitrate reduction, based on linear sweep voltammetries (Fig. 1, right) and constant potential electrolyses, were performed on an alloy of approximate composition $Ag_{30}Ni_{70}$, with a significant yet limited Ag content. The main observations from these tests are: a) lower overvoltages for nitrate reduction with respect to pure Ni; b) marked increase of reduction current with respect to both Ag and Ni, in a broad potential region; c) better selectivity to NH_3 production and lower H_2 evolution.

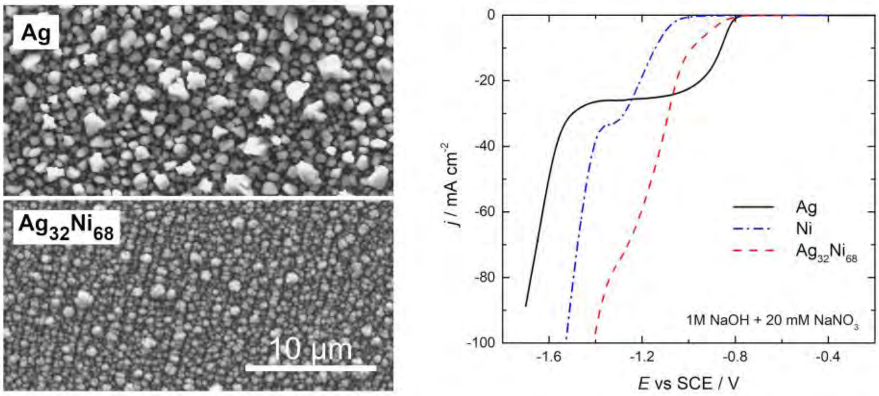

Fig. 1: SEM images of Ag and $Ag_{32}Ni_{68}$ samples from conc. chloride medium (left), and LSV of NO_3^- reduction on Ag, Ni and $Ag_{32}Ni_{68}$ cathodes in 1 M NaOH (right).

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Effects of Melamine Adsorption on Activity of Pt/Pd/C Core-Shell Catalyst

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In a NEDO project "Advanced Technologies for Reduction in Pt Usage (FY2015-19), we have developed highly active catalysts based on the core-shell technique. We have so far developed a new preparation method (the direct displacement (DD) method), which is suitable for mass production of Pt/Pd/C core shell catalysts as well as an activation method (the H_2-O_2 gas-switching method) and polydopamine coating for improving the durability[1-4].

One of the problems in the DD method is the parasitic formation of large Pd particles, which spoils the activity of the resulting Pt/Pd/C [4]. We overcame this problem by the use of an improved Pd core particles (Ishifuku Metal Industry) that have much less fine Pd particles, and obtained a very high mass activity (1,685A/g-Pt, 775A/g-PGM) after activation using high activation protocol (HAP, rectangular wave, 0.05 V (300 sec)-1.0 V (300 sec), 80°C, 50 cycles). Furthermore, we increased the Pd core loading from 30 to 46 wt% using Ketjenblack EC-600JD (1600 m^2/g), and obtained good MEA performance (0.1 mg-Pt/cm^2, 80°C) shown in Fig. 1. The performance at 1.0 A/cm^2 was 3.7 times higher than that of Pt/C catalyst; that is, it is comparable to the performance of Pt/C at a loading of 0.37 mg/cm^2. The performance at high current densities are significantly improved (2.0 A/cm^2 at 0.6 V) as well.

We developed a novel activation method, in which Pt surface is modified with N-containing organic compounds [5-7]. One example is shown in Fig. 2, where melamine molecules [5] were adsorbed on the surface of Pt/Pd/C. Without melamine adsorption, the mass activity was 1,460 A/g-Pt. After melamine was adsorbed, it increased to 3,625 A/g-Pt (x 11 of Pt/C, 1,673 A/g-PGM). Water adsorption on Pt(111) is a strong inhibitor for the activity for ORR. Melamine is weakly adsorbed on Pt surface, and suppresses the adsorption of water, which resulting in the high ORR activity shown in Fig. 2.

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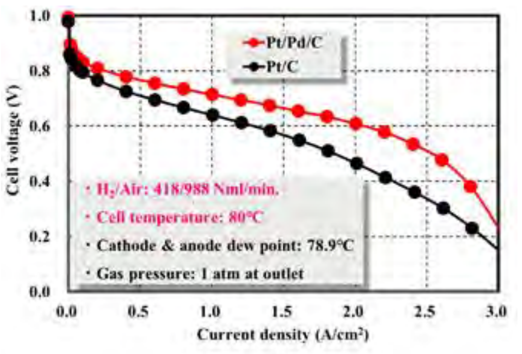

Fig. 1. MEA performance of Pt/Pd/C (0.1 mg/cm^2) and Pt/C (0.1 mg/cm^2) at 80°C.

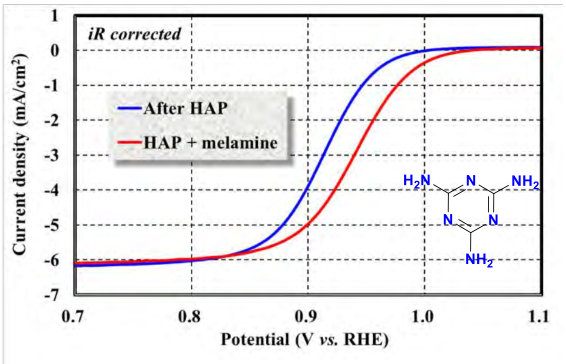

Fig. 2. Linear sweep voltammogram at Pt/Pd/C with and without melamine adsorption after HAP in 0.1 M $HClO_4$ at 25°C.

Effects of $Ti_3C_2T_x$ Nanosheets (MXenes) in the Electrocatalytic Activity of SnO_2/Ti Anodes for the Degradation of Methyl Red

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In recent years, electrocatalytic advanced oxidation processes have received growing attention for wastewater treatment. In this context, various metal oxide-coated anodes have been studied for anodic oxidation of pollutants in wastewater exhibiting excellent electrocatalytic activity. Among them, SnO_2-coated anodes have shown a high electrocatalytic activity for the generation of hydroxyl radicals ($^{\bullet}OH$) and ease of fabrication [1].

In addition, $Ti_3C_2T_x$ nanosheets (MXenes) are a two-dimensional material which application seems promising in batteries, supercapacitors and catalysis due to their high surface area and metallic conductivity [2, 3].

The present work aims to fabricate stable MXenes-SnO_2 electrodes by spin coating of a precursors solution on Ti substrates and to study the effects of the MXenes and cerium incorporation on the electrodes microstructure, electrocatalytic activity for the oxygen evolution reaction and the catalytic activity for the electro-oxidation of methyl red. The precursors solution contains MXenes particles, $SnCl_2$, $CeCl_3$, citric acid and ethylene glycol and after spin coating the electrodes are thermally treated in the presence of air.

The obtained electrodes are characterized in terms of morphology, chemical composition and crystallinity by scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), Raman spectroscopy and x-ray diffraction (XRD). The electrochemical behaviour and electrocatalytic activity are characterized by cyclic voltammetry (CV) and electro-oxidation of methyl red (MR) experiments.

Electrodes characterization indicates the formation of a SnO_2-TiO_2 film when MXenes nano-sheets were added to the precursor solution (MXenes-SnO_2/Ti electrode) and a Ce-doped SnO_2-TiO_2 film with additional cerium incorporation (MXenes-SnO_2-Ce/Ti electrode). Furthermore, the addition of MXenes nano-sheets led to the incorporation of Ti^{4+} ions into the lattice of SnO_2 crystals. CV curves demonstrated that the oxygen evolution reaction is restrained in the MXenes-SnO_2/Ti and MXenes-SnO_2-Ce/Ti electrodes. The maximum MR degradation rate was achieved using MXenes-SnO_2/Ti electrodes, whereas the minimum was obtained for the MXenes-SnO_2-Ce/Ti electrodes. The enhanced catalytic activity verified for the MXenes-SnO_2/Ti electrodes can be attributed to the generation of oxygen vacancies in the crystal lattice, which act as charge carriers and increase the electrical conductivity of SnO_2.

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Long-term Stability of Anion Exchange Membrane Fuel Cells Studied on Membrane Electrode Assemblies

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The anion exchange membrane fuel cell (AEMFC) is an attractive alternative to its acidic counterpart, the proton exchange membrane fuel cells (PEMFC), and has recently received increasing attention. In principle, they allow the use of non-precious metal catalysts thanks to the high pH of the electrolyte, which reduces significantly the cost in fuel cell systems. Through the development of new materials the performance of AEMFC has increased substantially enabling competition with PEMFC regarding begin of life performance. However, the long-term stability of AEMFC is one of the remaining challenges for this technology.[1-2]

The improvable stability under fuel cell operation is mainly related to the degradation of the anion exchange membrane (AEM) and the anion exchange ionomer (AEI), which were identified as crucial components in AEMFC. They are composed of nanostructured polymer backbones with positively charged functional groups, typically based on quaternary ammonium functionalities, distributed along the polymer chain. While their hydroxide (OH^-) conductivity has reached satisfying values, the most critical issue is that the molecular structure of the membrane itself decomposes due to the presence of the highly nucleophilic OH^-.[3] The nucleophilic attack is enhanced at low content of water coordinating the hydroxide ion which occur at high current density operation of AEMFCs.[4-5] These findings highlight the need of more stable polymer materials, characterisation techniques that enable stability studies under conditions simulating AEMFCs in operation and investigations of the long-term stability at single cell level.

In this contribution, the voltage decay over the operation time was investigated at the single cell level allowing the evaluation of the performance stability under fuel cell conditions. Membrane electrode assemblies (MEA) were prepared using different membrane materials and characterized by the application of developed test protocols. The degradation of polymer components was accelerated by the distinct application of harsh conditions. Possible degradation pathways of the MEA dependent on the applied parameters were enlightened by *in situ* electrochemical impedance spectroscopy and widespread *ex situ* testing at end of test conditions. Morphological changes were determined with µ-computed tomography and atomic force microscopy. Degradation products of the AEM and AEI were detected by ion chromatography of the exhaust water. Spectroscopic techniques were applied to investigate structural changes of the membrane. This combination of measurements under AEMFCs condition and distinguished analytical tools contributes to a more comprehensive understanding of AEMFC long-term stability.

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Low-temperature synthesis of nanocrystalline, halogen-doped $BaZr_{0.8}Y_{0.2}O_{2.9-\delta}$ proton conductor by the sol-gel method.

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Yttrium-doped barium zirconate (BZY) is one of the most promising materials for electrolytes in protonic ceramic fuel cells (PCFCs) in the intermediate temperature range (400-700ºC) due to its high proton conductivity in humid atmospheres and its good chemical stability against acid gases such as CO_2 in typical PCFC operation conditions. However, chemical stability may be further enhanced on incorporation of halogens, reducing the basicity of the perovskite-lattice. Employing conventional sintering techniques and powders, temperatures around 1700°C are required to obtain ceramic pellets with sufficient densification (> 95% relative density). Alternative methods such as sol-gel synthesis allow the preparation of the yttrium-doped barium zirconate powder at low temperature (700ºC) with higher reactivity. In this study, the $BaZr_{0.8}Y_{0.2}O_{2.9-x/2-\delta}M_x$ series (M = Cl, F and x = 0, 0.1) were prepared by a modified sol-gel method based on alkoxide routes in order to study the influence of the halogen dopant on both microstructural and electrical properties. Pellets and thin-films were obtained by a combination of dip-coating and sol-gel synthesis by low-temperature thermal annealing at 1000ºC, and single BZY phase without barium carbonate was obtained. The combination of sol-gel and dip-coating methods may be a promising alternative for the fabrication of BZY proton conductors.

Controlled electrodeposition of nanoscale n-Si/metal Schottky junctions for water dissociation

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Silicon (Si) is an attractive electrode material for manufacturing photoelectrochemical cells (PECs) because it has a small bandgap, it is very abundant and widely used in the photovoltaic industry. Nevertheless, using Si as a photoanode for oxygen evolution reaction (OER) is highly challenging as Si surface is particularly prone to deactivation by spontaneous oxidation and chemical etching. In order to solve this matter, conformal surface protection methods have been applied by several processes (e.g. chemical vapor deposition, atomic layer deposition, sputtering or evaporation[2]).

Recently, ourselves and others have reported that transition metals (Ni[1a,b], Fe[2] and Co[3]), electrodeposited on n-type Si from aqueous solutions. In the form of isolated nanoparticles (NPs) to create nanoscale Schottky contacts enable to perform OER for several hours under simulated sunlight at pH 14. Actual knowledge suggest that these surfaces behave according to the pinch-off model, which predicts a strong dependence of the NPs size and their respective spacings on the photoelectrode property[4][5]. However, the typical electrodeposition procedures that were used so far led to randomly-dispersed arrays of metal NP onto n-Si. Using this methods, the geometrical parameters of individual Schottky junctions and their respective spacing cannot be accurately controlled.

The lithographically patterned nanowire electrodeposition (LPNE) method combines basic photolithography steps with electrodeposition. It allows to fabricate high aspect-ratio nanowires vertically aligned on a substrate[6]. In this work, we adapted this process to n-Si wafers in order to create a series of photoanodes with controlled nanoscale n-Si/metal contacts. In this presentation, we will present this method and discuss our last results which aim to provide a better general understanding of these outstanding junctions.

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Preventing Thermal Runaway in Lithium-Ion Batteries through Functionalisation of Passive Materials and Components

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Lithium-ion batteries are widely used in portable electronic devices, electric vehicles and distributed energy storage systems due to their high energy density, high power density and light weight.[1-3] The safety concern is the main obstacle that hinders the large-scale applications of lithium-ion batteries in electric vehicles and energy storage systems. The cascading thermal runaway is the most catastrophic safety failure of lithium-ion batteries. Thermal runaway can occur due to the electrical abuse such as short circuit and overcharge/over-discharge, thermal abuse like exposure to excessive temperatures, and mechanical abuse like crush or penetration of the battery pack. It can release toxic and flammable gases, generate heat, cause fire and even explosion. For large-scale applications of lithium-ion batteries, the thermal runaway of one failed battery can cause a thermal cascade throughout the battery pack.

To prevent the thermal runaway in lithium-ion batteries, we functionalised the passive materials and components instead of the active materials to maintain the full choice of active materials and obtain enhanced safety and lifetime without compromising on power density, energy density or cost. The positive temperature coefficient of resistivity (PTCR) additives were introduced into battery electrodes to replace the conductivity additive (e.g. carbon black) or as coatings on the active materials. PTCR material exhibits a raised electrical resistance as the temperature increases. When the electrode temperature passes a threshold value, the PTCR embedded electrodes become non-conducting to interrupt electron pathways, suppress all electrochemical reactions and impede further temperature increases, thus preventing thermal runaway in lithium-ion batteries.

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Magnetron sputtered NiO thin films for sodium ion battery electrodes

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NiO thin film electrodes were successfully prepared by magnetron sputtering (MS) deposition under an oblique angle configuration (OAD). Intercalation of Na ions in the nickel oxide layers has been studied using electrochemical techniques (cyclic voltammetry, galvanostatic discharge-charge cycles and electrochemical impedance spectroscopy). Sample characterization before and after sodium intercalation has been carried out by SEM, micro-Raman, XPS, RBS and XRD measurements. The porous structure of the films is confirmed by electron microscopy evaluation. The increasing of the cycle's number leads to a continuous reduction of the discharge capacities due to some amount of Ni^0 and Na_2O produced during the discharge process remains in the electrode and does not participate in the charge process. Sodium half cells have shown a discharge capacity of 465 mAh g^{-1} after 16 cycles at 400 mA g^{-1} between 0.01 and 3.00 V (vs. Na^+/Na).

High-Efficient Cathode Catalysts of Li-CO_2/O_2 Batteries

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Li-O_2 battery and Li-CO_2 batteries hold high energy density of 3500 and 1876 Wh kg^{-1}, respectively, and are promising new generation of energy storage systems[1]. For the Li-O_2 battery, trace of CO_2 in air (environment) will result in inevitably the formation of side product Li_2CO_3, which leads to severe degradation of batteries and limits the cycleability. While the discharge products of Li-CO_2 battery are Li_2CO_3 and C[2]. Therefore, investigation of the properties of the Li_2CO_3 based on the Li-CO_2/O_2 batteries is significant for the rational design of cathode catalysts to enhance the cyclicity performance of of Li-CO_2 and Li-O_2 batteries. In this work, 3 different catalysts, Ru/NC，Ru/NiO@Ni/CNT and Pt/CNT were prepared based on consideration of the uniform distribution, the synergetic effect and the high activity of catalytic sites. The results demonstrated that the designed and prepared catalysts exhibit high activity for the decomposition of Li_2CO_3 and have significantly improved the cycleability.

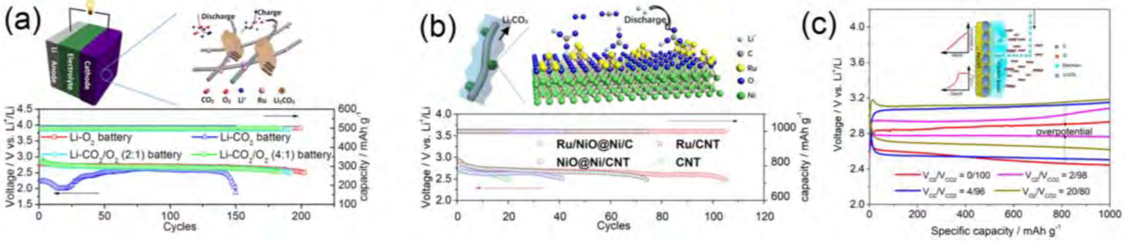

Figure 1 The performance of Li-CO_2/O_2 batteries with (a) Ru/NC, (b) Ru/NiO@Ni/CNT, Ru/NC, NiO@Ni/CNT, CNT and (c) Pt/CNT catalysts.

(1) Ru/N-doped carbon nanotube (Ru/NC) catalyst. It was prepared by solvothermal method. The Ru nanoparticles are uniformly distributed on the surface of NC (Figure 1a). The Li-CO_2/O_2 battery with this catalyst operated with $V_{CO2}:V_{O2}$= 4:1 presents an overpotential of 1.06 V and could be cycled smoothly for 184 cycles at 500 mAh g^{-1}. XRD and SEM characterizations reveal that the as-generated Li_2CO_3 can be effectively decomposed by the Ru/NC catalyst. Besides, with Ru/NC catalyst, the Li-CO_2/O_2 battery operate with different $V_{CO2}:V_{O2}$ ratios ($V_{CO2}:V_{O2}$= 0:1, 2:1 and 1:0) also show enhanced cycling stability of 200, 190 and 150 cycles, respectively.

(2) Carbon nanotube supported Ru/NiO@Ni catalyst (Ru/NiO@Ni/CNT). It was synthesized with Ru nanoparticles (~2.5 nm) anchored on the surface of core-shell structure NiO@Ni nanoparticles (~17 nm). The Li-CO_2/O_2 ($V:V$=4:1) batteries with Ru/NiO@Ni/CNT catalyst has delivered a long cycling life of 105 cycles at a cut-off capacity 1000 mAh g^{-1} with overpotential as low as 1.01 V, demonstrating a strong synergetic effect between the Ru and NiO species in electrocatalytic decomposition of Li_2CO_3 (Figure 1b). Density functional theory (DFT) calculations indicates that the formation O_2 is the rate determining step in RuO_2 promoted electrochemical decomposition of Li_2CO_3. Furthermore, the formation and decomposition process of Li_2CO_3 on Ru/NiO@Ni/CNT catalyst was illuminated at a molecule level by *in-situ* FTIRs spectroscopy.

(3) Pt/CNT catalyst. It was prepared by deposition of 2.5 nm Pt nanoparticles uniformly on CNT. DFT analysis indicates that the formation of O-O bond in Li-CO_2/O_2 battery and the generation of C-O bond in Li-CO_2 battery during Li_2CO_3 decomposition are the rate determining steps, respectively. When using Pt/CNT catalyst as cathode in the Li-CO_2/O_2 battery with 2% O_2 content, the ever lowest overpotential of 0.3 V and stability of 128 cycles at 1000 mAh g^{-1} have been achieved (Figure 1c). The formation (2.5 V) and decomposition (3.2 V) of Li_2CO_3 have been studied at molecular level using *in-situ* FTIR spectroscopy.

This study if of significance in development of highly efficient cathode catalysts of Li-O_2 batteries.

Acknowledgement: Financially supports from NSFC (21621091, 21875197, 21703182 and 21903001).

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Novel single-ion conducting polymer electrolyte for lithium-metal batteries

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Lithium-based batteries are now increasingly employed in portable electronic devices, (hybrid) electric vehicles (EVs) and stationary energy storage. This rapidly expanding list of potential applications and the consequent rise in number of battery cells needed demands for more efficient, safe and environmentally friendly battery systems. Among different battery technologies, polymer electrolytes are being intensively studied for use in solid-state lithium-metal batteries to power electronic devices, including EVs.[1-3]

In this work, the design of a new single-ion conducting polymer electrolyte is presented. The very facile synthesis is environmental-friendly and cost-efficient, involving only a very limited number of steps. The polymer electrolyte is based on a (commercial) polysulfone backbone with covalently tethered fluorinated side chains bearing the ionic function. The resulting single-ion conductor is blended with ethylene carbonate (EC). The chemical structure was confirmed by nuclear magnetic resonance (^{1}H-NMR and ^{19}F-NMR) spectroscopy. Following a comprehensive physicochemical and electrochemical characterization, revealing inter alia an electrochemical stability window of ca. 4.75 V and an ionic conductivity of $1.5*10^{-4}$ S cm^{-1} and $2.4*10^{-4}$ S cm^{-1} at 30 °C and 40 °C, respectively, the applicability of this electrolyte for high-energy Li/NMC$_{622}$ cells was evaluated. The cells provide a specific capacity of more than 160 mAh g^{-1} at C/20 and stable cycling at C/5, indicating that this new electrolyte may serve the realization of intrinsically safer, high-performance lithium-metal batteries.

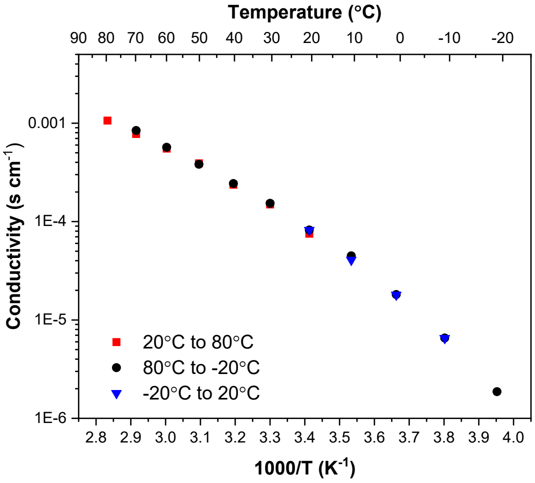

Fig. 1. *Ionic conductivity of the single-ion conducting polymer electrolyte comprising 37.5 wt% of EC as a function of temperature.*

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New models for the Electrochemical Double Layer of the Pt(111)-Aqueous Electrolyte Interface

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Atomic/molecular level understanding of the double layer, interfacial water structure such as organization and orientation, H-bonding network at the metal-electrolyte interface is of utmost importance for fundamental electrochemistry as well as for technological applications[1–3]. The interfacial water structure at the metal-electrolyte interface is the most important part of the double layer structure which governs all kind of interfacial physio-chemical properties and processes. Pt is the most studied and applied metal in energy conversion, electrocatalysis, and electroanalytical sensing. The double layer structure of Pt is still incompletely understood although it has been investigated for more than 50 years. Recently, we discovered the minimum of the Gouy-Chapman capacitance on Pt (111) for the first time and directly identify the potential of zero charge of Pt(111)[4], which is an important intrinsic property of an electrode material. Similar experiments were demonstrated to observe the GC capacitance and pzc of Au(111) which is in good agreement with the literature[5]. The inner layer and diffuse layer capacitance of Pt(111) are significantly higher than that of Au(111) and mercury. By comparing the diffuse layer capacitance of Pt(111), Au(111), Ag(111) and Hg, we understand that Pt(111) is better screened by the ions (electrolyte) at the interface (outer Helmholtz layer). This is due to the interfacial water-ion interactions following reverse Hofmeister series which is investigated by using non-specifically adsorbing anions (e.g. perchlorate, fluoride, methanesulfonate) and their concentration contributing to the double layer capacitance of Pt(111)[6]. The presentation will discuss these new data in detail and will suggest a new model of the Pt(111)-electrolyte interface.

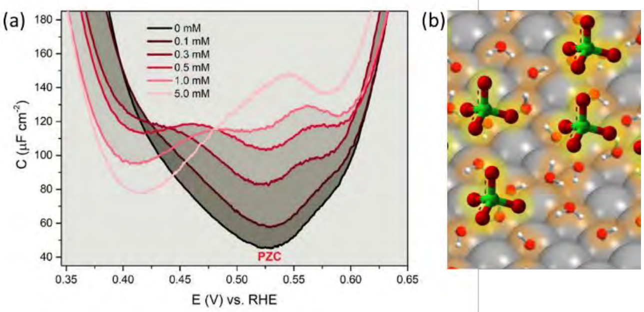

Figure 1. (a) Capacitance curves of Pt(111) in $HClO_4$ electrolyte (pH = 4) showing GC capacitance minimum at PZC (b) schematic of Anion-water (interfacial) interactions on Pt(111).

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Voltammetry of cobalt(II) complexes with naturally present organic ligands in seawater

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Cobalt (II) as an essential element and important for biochemical processes in the marine environment, is bioavailable in its dissolved form. At present it is known that cobalt in seawater is partially, but strongly complexed to natural organic ligands (binding place for cobalt is very possible a nitrogen-containing functional group). Dissolved cobalt(II) is biologically important element for marine organisms (for their biochemical and physiological functioning). Despite its abudance in oceans, dissolved Co^{2+} is present in low concentrations, $<10^{-9}$ mol L^{-1}, mostly as soluble organic complex. [1,2] Electrochemical characterization of cobalt (II) complexes in model aqueous solution (0.55 mol dm^{-3} NaCl) was performed using square wave and cyclic voltammetry on mercury drop electrode.

Results on complexation and electrochemical reaction mechanisms of cobalt (II) complexes with 4-nitrocatechol, humic acid, glutathione and 1,10-phenanthroline, as ligands appearing in the marine system, will be presented. All used ligands are biologically important molecules. Catecholates, ortho-dihydroxybenzene and 4-nitro-dihydroxybenzene are present as a structural part of complex marine ligands (humic acid, siderophores, etc.). Humic substances as heterogeneous biomolecules are a characteristic component of the dissolved organic carbon (DOC) pool important for phytoplankton communities in seawater. [3] Glutathione is present in eukaryotes and some prokaryotes (cyanobacteria and purple bacteria) and makes up > 90 % of non-protein thiols in plants and algae [4], while 1,10-phenanthroline is an inhibitor of metallopeptidases. [5]

All of these Co(II) complexes are electroactive and give a reduction response on a voltammograms (square wave and cyclic) from E_p = -0.9 to -1.1 V.
Mechanisms and stability constants of complexes were determined. While reduction reactions with 4-nitrocatechol and humic acid were irreversible, reduction reactions with glutathione and 1,10-phenanthroline showed reversible/quasireversible behavior. Using CLE/ACSV method were calculated stability constants for Co(II)4NC and Co(II)HA_2 complexes, (log $K_{Co(II)\,(4NC)2}$ = 21.86 (pH = 8.2), log $K_{Co(II)\,(4NC)\,2}$ = 21.11 (pH)= 6.5), log $K_{Co(II)\,(HA)2}$ = 11.32 (pH = 8.2)). For other complexes calculations are in process.

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Environmentally Friendly Treatment of Textile Using Electrochemically Generated O_3-water with UV Irradiation

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Recently, application of advanced oxidation technologies (AOTs) for environmental purification have received growing attention [1]. Especially electrolysis with boron-doped diamond (BDD) electrodes make it possible to generate various highly active oxidants such as O_3 which can oxidize aqueous contaminants [2]. In this study, we introduce recent studies about environment-friendly "AOT-treatments" of textile by using of O_3-water with UV irradiation instead of conventional treatments (scouring and bleaching) with environmentally persistent reagents. Fig. 1 shows the photographs of cotton bleaching by AOT. Cotton fabrics were treated by O_3-water (1.0 ppm, 1.5 L/min, continuously generated from tap water) with UV irradiation (170 mW/cm^2 @310-380 nm). After treatments, the fabrics were dried under room temperature and analyzed by reflection spectra. Fig. 2 left shows the reflection spectra and photographs of cotton fabrics. After 60 min of AOT, the spectrum and whiteness of the cotton are almost the same with conventional chemical-bleached one. But the only problem is "color reversion" by ironing (heating around 200°C). Heating of oxidized cellulose generates conjugated systems and yellow color (Fig. 2 right, green line). However, we found that reduction of oxidized cellulose by rongalite can prevent color reversion (Fig. 2 right, red line). Therefore, AOT-treatment is attractive to reduce energy consumption and cut waste in the fabric processing.

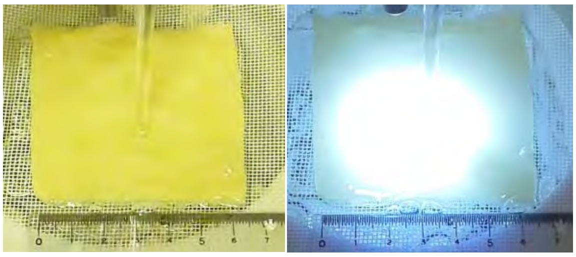

Fig. 1. Cotton bleaching by O_3-water treatment (left) and O_3-water with UV irradiation (AOT, right).

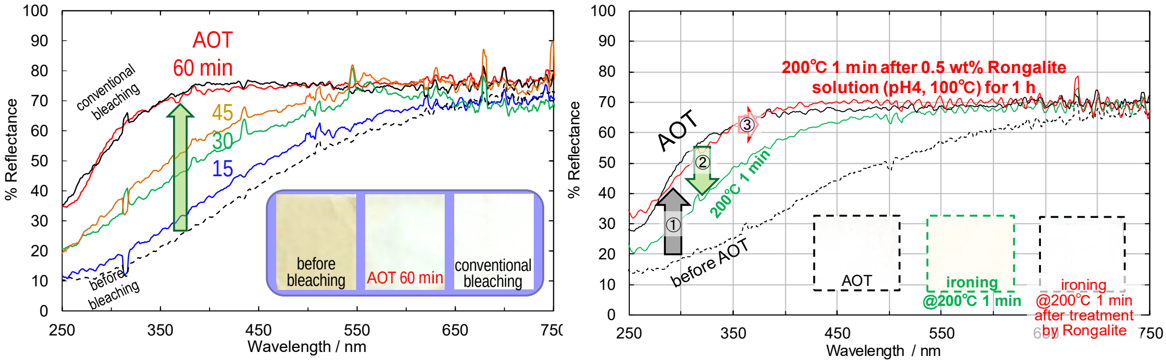

Fig. 2. Reflection spectra and photographs of cotton fabrics. (left) Comparison of AOT and conventional chemical bleaching. (right) Effects of rongalite-reduction for preventing of color-reversion by heating.

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Spatiotemporal Confinement of Redox Reactivity at the Silicon–Electrolyte Interface by a Light Stimulus

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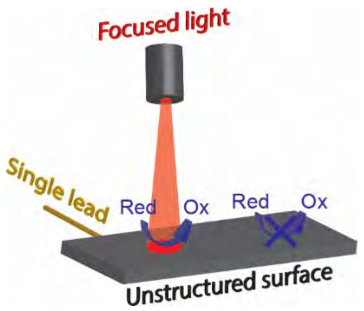
Chemical reactivity is often discussed and studied in the context of mixing bulk reactants in a homogeneous media. However, specific applications require confining a chemical reaction, or a cascade of reactions, at a precise location and at a certain moment. For instance, localizing chemical reactivity is required to maintain life – a state of low entropy or high organization – and all biological systems rely on chemical triggers that are accurately addressed and confined in space and time. Mimicking such natural processes by triggering or stopping chemical reactions in precisely selected areas have answered everlasting questions of molecular and cell biology.[1] The spatiotemporal control of chemical reactions is also a central feature to man-made systems; many current technologies, ranging from biomedicine to photolithography pivots around means of spatiotemporally controlling chemical reactivity.[2] However, triggering transient chemical changes at a specific microscopic site over a macroscopic substrate remains challenging.



Focusing mainly on heterogeneous redox chemistry, we have shown that chemical reactions can be addressed with spatiotemporal control on a semiconductor surface without the need of physical probes or photochemical reactions.[3] For this, we take advantage of the property of semiconductors to generate charge carriers upon illumination. Driven by an electric field, the photogenerated charge carriers are transferred to redox species in the solution in contact with the semiconductor surface. A focused light stimulus is used to generate localized transient fluxes of charge carriers, hence triggering a chemical change in the species near the interface with spatiotemporal resolution. We developed an optical/electrochemical system to localize the light stimulus and hence the chemical reactivity.[4]

We demonstrate the versatility of this "light addressable" principle first by assembling patterns of nanoparticles with adjustable morphology and interparticle spacing over space.[5] Nanoparticle arrays are formed in a single-step, within seconds, with a resolution of few microns, and without the need of physical masks or templates. Furthermore, shining light on a semiconductor to localize a redox reaction was used to interrogate its surface activity.[4] The photocurrent recorded is linked to the local surface activity, and was used to construct redox chemical microscopy images. Driving and reading redox reactions over space using light was also explored in the context of chemical analysis. Analytical models were developed to interpret the photocurrent – voltage data acquired in photoelectrochemical systems.[6-7]

Our latest research focuses on the spatiotemporal control of chemiluminescent reactions. Unlike fluorescence, spatiotemporal control of chemiluminescence is an unmet challenge. As a result, fluorescence remains the dominant microscopy technique. However, major drawbacks of fluorescence are absent in chemiluminescence, potentially giving it a significant advantage over fluorescence in the field of microscopy. By means of a focused light stimulus delivered to the sample from the opposite side under analysis we provide a strategy for removing interference between excitation and emission lights, light-induced sample damages, photobleaching and autofluorescence, all commonly encountered in fluorescence microscopy.

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Evidences of the Space Charge Layer Formation in Li-Conducting Solid Electrolytes

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The traditional Lithium Ion battery (LiB) technology has approached its maximum in energy and power density in the last years. Several emerging new generation material systems and technologies such as All-Solid-State Batteries (ASSB) have been proposed recently. The traditional liquid electrolytes of LiB are flammable, as they are based on organic solvents and do not provide mechanical strength to inhibit the growth of Lithium metal dendrites, which is the most important reason why the holy grail of battery technology, namely lithium metal anodes, have not been implemented in commercial systems. Pure lithium metal anodes have the highest theoretical energy density (3860mAh/g) and the lowest negative electrochemical potential of 3.04V (versus standard hydrogen electrode).

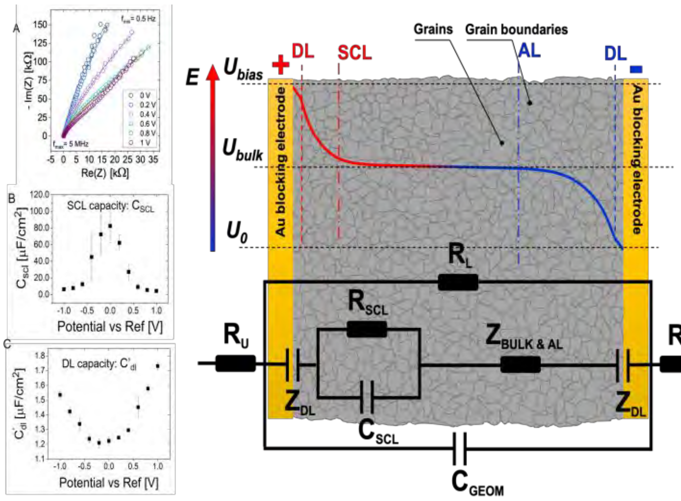

Fig 1: A) Impedance spectra for Au/LICGC[5]/Au cell under potential variation B) Space charge capacitances in the order of several dozens of microfarad. C) Double layer pseudo-capacitance with bias dependency. Right) Physical and Electrical Modell for a Solid Electrolyte showing the contributions of double (DL), accumulation (AL) and space charge layer (SCL) to the impedance equivalent circuit.

While stand-alone solid electrolytes, such as LATP and LAGP are stable in air, even with humidity and against metallic lithium a series of challenges are posed by the interface towards electrode materials. While highly planar interfaces of polished LAGTP glasses suffer from void formation upon cycling[1] and chemical decomposition is observed for sulfide solid electrolytes[2], a more underlying phenomena the so-called space charge layers have been theoretically predicted but not observed to date. A thermodynamic model[3], although neglecting direct coulomb interaction, suggest charge layers with a thickness of several hundred nanometers, while an electrochemical model[4] predicts a thickness of single nanometers. In this work, we present evidence of space charge layers in Ohara Glass[5] upon polarization in blocking conditions using Impedance Spectroscopy. An elaborated equivalent circuit, including two different charge accumulation (pseudo) capacitances, is used to fit impedance spectra to obtain the capacitances, and thus dielectric properties and thicknesses can be calculated. The space charge layer thickness is approx. 60nm leading to a non-negligible interface resistance.

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Electro photo sensitive smart nanobiocomposit based on DNA super coil/metal/aptamer spiral lattice for early detection of CTC

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Early detection of breast cancer is so much important to treatment of patient. Nano device with multiple application and special molecular properties have crucial role in developing of nanotechnology and nano biosensors. In this study, a new effective and conducive DNA super coil/metal/aptamer nanostructure and nanodevices designed and fabricated. DNA based nanospiral lattice fabricated with DNA super coil hybridized with Ag nanoparticles. This nanosubstrate immobilized with specific aptamer by non-covalent and covalent interaction. These self-assembled hybrid nanostructure could be used in nanowire, nanocapacitor and nanobiosensor fabrication. Hybrid and self-assembled nanostructure fabricated by region selective covalent combined between aptamer and DNA super coil/metal Nano structure. These hybrid nanostructures have different electrochemical properties compare of alone DNA super coil/metal and DNA super coil/metal/aptamer and also hierarchical DNA super coil/metal/aptamer/CTC. Electrochemical behavior of hierarchical hybrid DNA/nanostructures are studied by cyclic voltammetry and impedance spectroscopy technique. DNA super coil/metal/aptamer wire shaped nanostructure utilized for bio sensing of breast cancer CTC. Results showed DNA super coil/metal/aptamer hierarchical and self-assembled nanostructure is good candidate for biosensor fabrication. Exactly, DNA super coil/metal/aptamer wire shaped nanostructure used for BC CTC molecular biosensor.

Keywords: DNA based nanodevices, CTC biosensor, and DNA super coil/metal/aptamer.

Assessment of Electrochemical Reactors for the Removal of Sulphur Dioxide and Production of Sulphur from Synthetic Effluents

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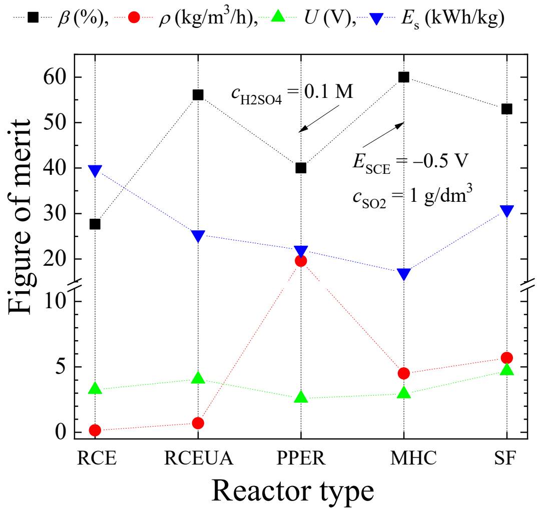
The combustion of fossil fuels for energy production and also several manufacturing processes produce sulphur dioxide as a gaseous effluent, which represents a deleterious agent for the environment requiring its treatment. Electrochemistry represents an interesting alternative for the abatement of the contaminant,[1] being desirable its transformation into useful species with commercial value. This concept can be achieved by electrochemical reduction of sulphur dioxide to colloidal sulphur, which is required for the fertilizer production and also in cosmetics, photographic, soap and dye industries. Additionally, the reduction of sulphur dioxide can also generate secondary compounds such as the polythionates, which present also practical applications.

The main issue for the electrochemical sulphur production is the passivation of the cathode due to its surface is covered with an insulating layer of sulphur which restricts the flow of current. Accounting that the reduction of sulphur dioxide in an acidic solution is mass-transfer controlled working under limiting current conditions in a narrow range of potentials,[2] it is inferred that the electrochemical reactor must have two-dimensional electrodes with good mass-transfer conditions. The reactors considered here are: rotating cylinder electrode, RCE, rotating cylinder electrode with ultrasound assistance, RCEUA, parallel-plate electrochemical reactor with a double convergent flow, PPER, modified hydrocyclone, MHC, and electrochemical reactor with decaying swirling flow, SF. The figure on the left-hand side compares parameters that characterise the performance of these reactors for the production of colloidal sulphur given by the mean values of: current efficiency, β, space time yield, ρ, cell potential difference, U, and specific energy consumption, E_s. One of the most relevant figures of merit is the space time yield showing the best value for the PPER. However, this reactor presents as a relevant problem the removal of the insulating layer of sulphur from the cathode surface. The rotating cylinder electrode shows a lower value of space time yield and the passivation can be avoided with application of ultrasound, improving the reactor performance. Reactors based on the modified hydrocyclone or swirling flow concepts present similar values of space time yield and specific energy consumption without cathode passivation in both cases due to the impingement effect of the helical flow. In the reactor SF it was used a large interelectrode gap, 24.15 mm, which contrasts with that for the MHC, 7.25 mm. In the design of the reactor with swirling flow, it has been privileged at the inlet an expansion swirl flow in order to improve the mass-transfer conditions. However, in counterpart the large interelectrode gap increases the reactor volume decreasing the space time yield and at the same time enlarges both the ohmic drop in the electrolyte and the cell potential difference, U, increasing the specific energy consumption. Thus, for the SF case the interelectrode gap can be further optimised for industrial applications. Then, it is concluded that the equipment with swirling flow represents the best option.



Working conditions: single phase flow, 5 g/dm^3 SO_2 in 0.5 mol/dm^3 H_2SO_4. E_{SCE} = –0.7 V. T = 30ºC. Unless otherwise is stated in the figure.

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Novel cell design for operando pressure measurements of Li-ion battery materials

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Operando pressure monitoring of Li-ion batteries has been identified as one of the most important predictors of the cycle life of the battery [1,2]. This is because the formation of very small amounts of gases during the operation of Li-ion batteries, or irreversible changes in electrode volume, can have very detrimental effects in the battery performance. Unfortunately, highly sensitive monitoring of pressure changes in Li-ion batteries is only available for commercial or pouch cell configurations, which are not available in many research laboratories and require large amounts of materials to produce large electrode sheets for their fabrication.

Here, we present a novel cell design (Figure 1) that is cheap and readily available to any laboratory, and requires very small amounts of materials to fabricate the electrodes. The cell is simple and uses standard Swagelok parts that are commercially available, thus providing an advantage with respect to previous approaches [3,4]. The cell also provides unprecedented sensitivity for operando pressure measurements, which is achieved by minimizing the gas headspace volume. We illustrate the application of this novel cell design for the operando pressure measurements of $LiFePO_4$ and graphite in Li half-cell configurations, and we show that the results reveal the reversible changes in electrode volume associated to Li-ion insertion/extraction processes, as well as the amount of gases evolved during the formation of an SEI on graphite. Due to its simplicity and high sensitivity, we believe that this new cell design is ideally suited for screening novel materials/formulations for Li-ion battery applications.

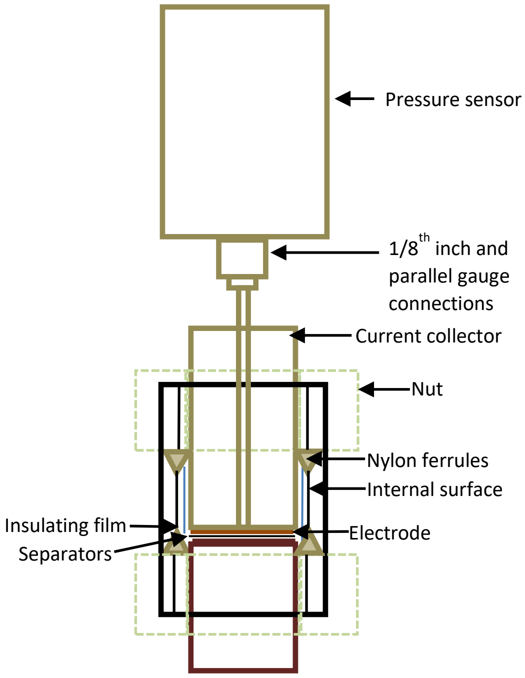

Figure 1. Sketch of novel and simple cell design for operando pressure measurements of Li-ion battery materials. By minimizing the connections between the cell and the pressure sensor, the gas headspace volume is kept at a minimum (1.9 ml in a one-inch diameter Swagelok cell).

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Dot-shaped cathode catalyst layer for improvement of mass transfer in toluene direct electro-hydrogenation

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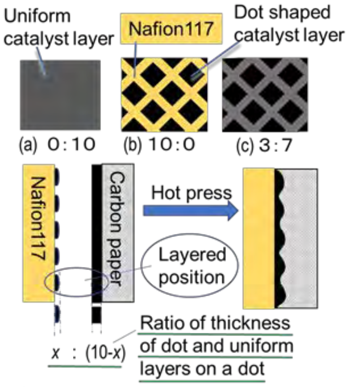
Introduction

Recently, the large-scale storage and transportation of hydrogen as secondary energy has been required for effective utilization of fluctuated and uneven distributed renewable energy. Toluene (TL)/ methylcyclohexane (MCH) organic hydride system is one of the candidates of hydrogen energy carrier. To improve the energy conversion efficiency for TL hydrogenation, we have studied direct hydrogenation of TL with water decomposition electrolyzer using proton exchange membrane.[1] To reduce the cell voltage and increase the current efficiency, we applied fine mesh anode based on ca 1.2 mm of strand width expanded metal. The ultrafine mesh anode based on sintered titanium fiber porous plate drastically reduced cell voltage. However, it decreased Faraday efficiency at the same tine. Uniform MCH layer, which was produced in the cathode catalyst layer with uniform structure of the anode, might block TL mass transfer into the catalyst layer. In this study, to improve TL mass transfer into the catalyst layer, the catalyst layer stacked for the dot shape and the uniform surface coating had been investigated.

Experimental

Figure 1 shows the structure of catalyst layer. The dot shape catalyst layer was formed on a proton exchange membrane (Nafion®117, DuPont), and uniform surface catalyst layer was formed on carbon paper (35BC, SGL carbon ltd.) using PtRu/C (TEC61E54, Tanaka Kikinzoku Kogyo). Catalyst metal loading was 0.75 mg cm^{-2} for the layered position. Thickness ratio of dot and uniform layers was indicated as *x*: (10-*x*). The anode was ultrafine mesh DSE® (De Nora Permelec, Ltd.). As a comparison, conventional fine mesh type DSE® was used. The anode and cathode compartments were circulated 1 mol dm^{-3} H_2SO_4 and 10% TL/MCH, respectively. The electrochemical measurements were conducted for the linear sweep voltammetry, the electrochemical impedance spectroscopy, the chronoamperometry to determine current efficiency at 60ºC.



(d) Cross-section of layered catalyst layer

Fig. 1 The structure of cathode catalyst layer.

Results and discussion

Figure 2 shows the cell voltage and current efficiency as a function of current density for various cathode structure. The low cell voltages with the ultrafine mesh anode are almost the same with various cathode catalyst layer structure compared with the cell voltage using the fine mesh anode. At this moment, the current efficiency improved with the dot layer structure, and 3:7 showed the highest in these structures. Cathode potential of 3:7 at a constant current efficiency was the lowest in these structures. From these results, the selectivity of hydrogenation should not be controlled by kinetics of charge transfer of the catalyst, but strongly affected by mass transfer process of TL in the catalyst layer. In this study, the optimized shape catalyst layer was 3:7.

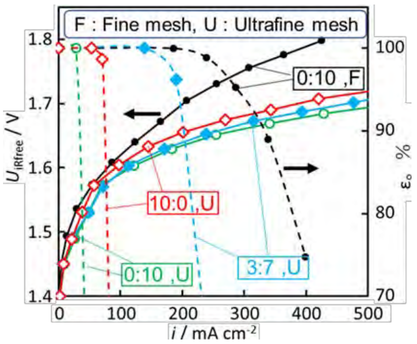


Fig. 2 Cell voltage (solid lines), and current efficiency (dashed lines) as a function of current density for x=0 (○, ●), and x=10 (◇) and x=3 (◆) shape cathode with each anode.

Acknowledgements

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Bifunctional H-Bonding Cross-Linked Polymeric Binders for Silicon Anodes of Lithium-ion Batteries

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Binders play a crucial role in the cohesion of active materials and conductive additives together onto the current collector.[1] The traditional PVDF binder with weak Van der Waals force could not maintain the electrode integrity of Si-based anodes. Therefore, strongly adhesive polymeric binders are required for enduring the severe mechanical stress derived from the large volume change. Basically, the optimal binder for Si-based anodes should have excellent bulk property, such as high chemical and electrochemical stability, suitable adhesiveness, strong ion/electron conductivity, functional group for self-healing, cost-effectiveness, and environmental friendliness.[1,2] Recent reports mainly focus on the bulk properties of binders to improve the mechanical characters and electrical conductivity of Si-based anodes. Nevertheless, the adhesion ability and functional mechanism of binders with Si active materials as well as with current collector are also important to maintain the electrode integrity and avoid the electric contact loss, whereas this problem is rarely investigated.

In the present study, we designed the H-bonding cross-linked polymeric binders (CMC-co-SN), through a consideration of the binders that should have excellent bonding interaction with Si active materials and copper (Cu) current collector while the preparation route is simple and low-cost. The preparation of the CMC-co-SN binders was carried out by in-situ thermopolymerization of chain-typed carboxymethylcellulose sodium (CMC) with sulfur-containing polymer (SN) during the drying processes of Si-based electrode disks. The obtained CMC-co-SN binders possess the bifunctional role (Fig. 1a) with Cu current collector and Si active materials through covalent bonding (-S-Cu-) and multi-hydrogen-bonding (-OH, -C=O, =S) forces, respectively. When served as binders to micro (1-5 μm) (M-Si) and nano (~50 nm) (N-Si) Si particles (Fig. 1b), the Si anodes exhibited high initial coulomb efficiency, 91.5% for M-Si and 83.3% for N-Si, and good cycle life, 1121 mAh g^{-1} for M-Si after 140 cycles and 1083 mAh g^{-1} for N-Si after 300 cycles, respectively. CMC-co-SN binders could be expanded to SiO and Si/C electrode materials, which also exhibited good electrochemical performance. The results demonstrated that the H-bonding cross-linked polymeric binders provide a novel strategy to improve the electrochemical performance of Si-based anodes through the bonding force of binders with active materials and current collector to maintain the electrode integrity and avoid the electric contact loss.

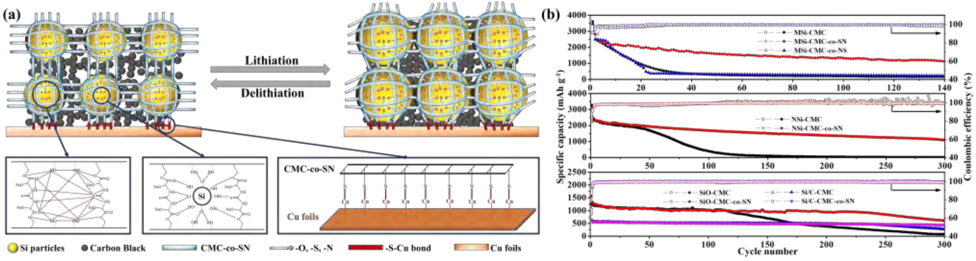

Fig. 1 (a) Schematic visualization of H-bonding cross-linked polymeric binders for Si anodes during cycling and the difunctional bonding effects with Si active materials and Cu current collector, (b) the corresponding cycling property and coulombic efficiency of M-Si and N-Si anodes.

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Oxygen Reduction Reaction on Te-modified Pt(111) Electrodes: Enhanced Electrocatalysis and Surface Charge Effects

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Chemical modification of electrode surfaces can strongly influence their electrocatalytic activity and the charge-transfer processes at electrified interfaces, and therefore it is one of the most common methods for the design of new electrocatalysts for different applications. In relation to the oxygen reduction reaction (ORR), an approach based on molecular patterning of platinum surfaces with cyanide adsorbates that can efficiently block the sites for adsorption of spectator anions with the ORR remaining unhindered was used for the rational design of cathode electrocatalysts with potential use in any environments containing strongly adsorbing anions [1]. In this work, it has been observed for the first time a similar enhancing effect towards the ORR by Pt(111) surfaces modified with different coverages of Te adatoms. In addition, the surface charge modification by the Te adlayer and its effect on the ORR electrocatalytic behavior can provide useful information about the mechanism of this reaction.

The ORR on Te-modified Pt(111) electrodes has been studied in $HClO_4$, H_2SO_4 and H_3PO_4 acidic solutions by using hanging meniscus rotating disc electrode configuration. Te was irreversibly adsorbed on Pt(111) [2]. While adsorption of Te-adatoms on Pt(111) progressively shifts towards less positive values the ORR reaction onset for $0 < \theta_{Te} < 0.25$ in 0.1 M $HClO_4$ solution (Fig. 1A), in 0.05 M H_3PO_4 and 0.05 M H_2SO_4 solutions a positive catalytic effect has been pointed out (Fig. 1B), interpreted in terms of a competitive adsorption-desorption mechanism involving replacement of adsorbed sulfate or phosphate species by Te adatoms. In addition, a displacement towards more positive values of the inhibition potential of the ORR is observed when increasing Te coverage (Fig. 1A), which is related to the modification of the surface charge and suggests that H_2O_2 intermediate is participating in the mechanism [3]. Measurements at higher pH values supply more information about the ORR bifurcation mechanism.

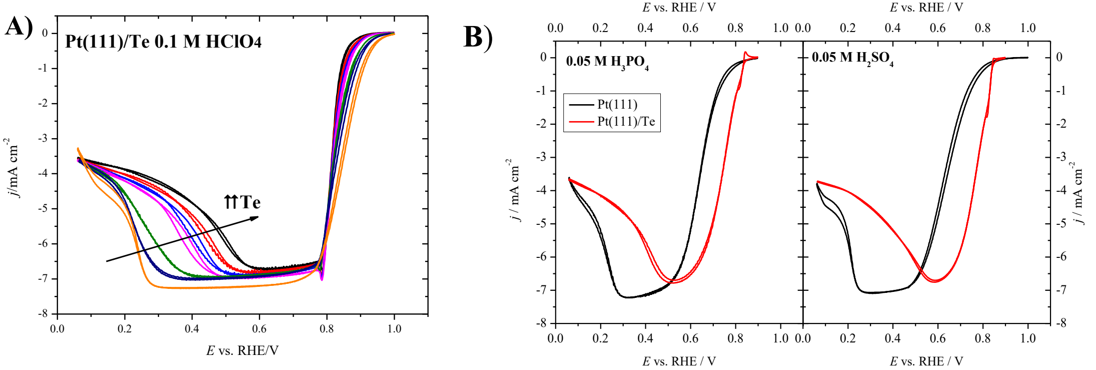

Figure 1: (A) Cyclic voltammetry profiles for the ORR in 0.05 M H_3PO_4 (top) and 0.05 M H_2SO_4 (bottom) on unmodified and Te-modified Pt(111) surface. (B) Cyclic voltammetry profiles for the ORR in 0.1 M $HClO_4$ on Pt(111) with increasing coverages of Te. Scan rate: 50 mV s^{-1}. Rotation rate: 2500 rpm.

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Electrochemical Activation of Expanded Mesocarbon Microbeads Using Polyurethane-Crosslinked Polyacrylic Acid as a Binder for High-Voltage Symmetric Supercapacitors

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The expanded mesocarbon microbead (EMCMB) is successfully made from MCMB through a combination of oxidation and thermos-expansion treatments, which shows excellent capacitive performance in the $TEABF_4$/PC solution after the electrochemical activation in the positive and negative potential regions. The purpose of the acidic oxidation process is to generate various oxygen-containing functional groups attached onto carbon atoms in the graphene layers. These groups were able to be removed in the gaseous form (i.e., CO and CO_2) during the thermal expansion process, which were expected to conquer the van der Waals force between graphene layers. Consequently, this effect leads to expanded/exfoliated graphene layers. MCMB, an artificial graphite, shows a very strong peak of facet (002), which refers to a d_{002} interlayer spacing of 0.335 nm, same as the typical interlayer spacing of graphite. By the Scherer's equation, the L_c and L_a values of MCMB are calculated to be 74.73 and 65.01 nm, respectively. After the oxidation and thermal expansion processes, the crystallinity of the expanded MCMB (EMCMB) decreases dramatically. The d spacing between graphene layer within EMCMB is distributed from 0.335 to 0.37 nm. In addition, the L_a value of EMCMB was estimated to be 8.77 nm, indicating that the crystal size of graphite has been cut down after the oxidation-expansion treatments.

To increase the energy of supercapacitors (SCs), the EMCMB is chosen to be electrochemically activated in 1 M tetraethylammonium tetrafluoroborate in propylene carbonate ($TEABF_4$/PC). The electrochemically activated EMCMB is able to be charged and discharged reversibly in a wide potential range between -2.6 and 1.4 V (vs. Ag/$AgNO_3$). Consequently, a 4 V and symmetric SC with good capacitive performances in 1 M $TEABF_4$/PC is constructed by such electrochemically activated EMCMBs, greatly enhancing the energy density to 77 Wh kg^{-1} on the basis of the total mass of EMCMB on both electrodes.

The electrochemical activation is a common technique enhancing the capacitive performances of carbons in high-voltage supercapacitors while volume expansion during the activation process often makes the active materials detachment, dropping the capacitance. In this work, the KOH-neutralized polyurethane-crosslinked-polyacrylic acid ($PUPAH_{10-x}K_x$) polymers are proposed to replace the polyvinylidene fluoride (PVDF) as a binder for expanded mesocarbon microbead (EMCMB) electrodes to buffer the volume expansion. The effects of binder rheology, morphology and neutralization degree on the capacitive performance of EMCMB are investigated. Introducing $PUPAH_6K_4$ with moderate viscoelasticity to EMCMB forms an expansion-buffering electrode and promotes the electrochemical activation process. In addition to a shorter activation time, EMCMB-$PUPAH_6K_4$ presents a maximal specific capacitance than others. The above results indicate that the specific capacitance of activated EMCMB electrodes is not directly proportional to the electrochemical activation time. Therefore, PUPAH neutralized with KOH changes the binder properties, affecting the charge storage characteristics of the resultant EMCMB coatings [1].

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Understanding pH and charge effects in the HER/HOR on platinum single crystal electrodes.

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An adequate description of an electrochemical process requires to understand how the different parameters that are governing the reactivity of the electrodes affect a given electrochemical reaction. For this reason, numerous studies are devoted to investigating the effects on the electrochemical reactivity of the surface structure and composition of the electrode as well as the nature of the solution. However, other parameters such us surface charge, which also can play a significant role, are often overlooked. In this communication, the effect of surface charge and the solution pH on the hydrogen evolution and oxidation reactions (HER/HOR) on platinum will be investigated. Platinum is probably the most active pure metal for these reactions. This is especially true in acidic solutions. However, the activity of the HOR on platinum decreases two orders of magnitude in alkaline media. In order to understand these differences, the HER and the HOR were studied under near neutral pH conditions in the absence of anion specific adsorption. The selected buffered solutions allow establishing reliable trends in the activity from acidic to alkaline solutions from which conclusions can be obtained. Single crystal electrodes, namely, Pt(111), Pt(100) and Pt(110), have been used in the electrochemical measurements and DFT calculations. For the HER, it was found that the effect of pH is almost negligible in the studied pH range (figure 1, left panels). These results indicate that the ionic composition and pH of the solution has not a significant effect on the HER. Thus, the concentration of protons, which is the reactant for the HER, does not limit this reaction under near neutral pH conditions. By contrast, the HOR was found to be pH sensitive mainly on Pt(111) and Pt(100) (figure 1, right panels). The major difference in the experimental conditions at which these reactions take place are the electrode charge. As the solution pH increases, the potential region at which the HER/HOR reactions takes places shift to more negative potentials in the SHE. Thus, the electrode charge becomes increasingly more negative. With the aid of density functional theory calculations, the effect of the increasing negative surface charge on both reactions is untangled.

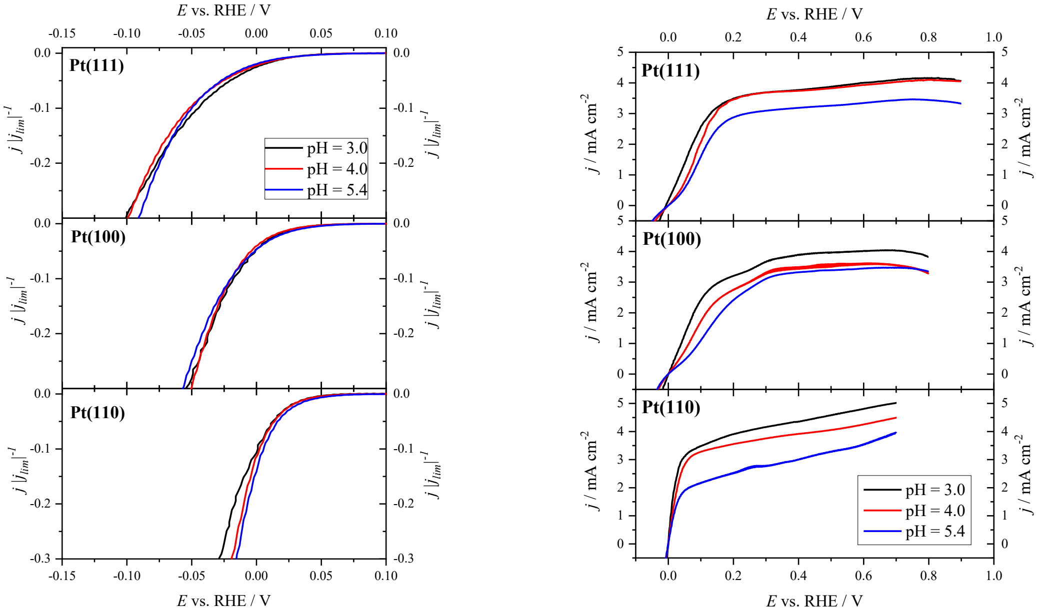

Figure 1. Effect of the solution pH in the activity of the HER (left panels) and HOR (right panels) for the different single crystal electrodes.

Surface charge and interfacial acid-base properties.

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It is well documented that Pt(111) electrodes in contact with 0.1 M perchloric acid solutions saturated with CO_2 show spectroelectrochemical signals associated to adsorbed bicarbonate and carbonate anions 1]. The relative intensities of the absorption peaks at different pH and applied potential can be used to determine the interfacial pK_2 of carbonic acid, which results considerably smaller than in solution phase, irrespectively of the assumptions made in the analysis of data [1, 2]. The study on the Pt(111) electrode benefits from the fact that CO_2 is not reduced to adsorbed CO on this surface, thus enabling to determine the necessary coefficients related to the adsorbed carbonate and bicarbonate species through a simple interfacial mass balance which involves the consumption of dissolved CO_2.

On other Pt(hkl) structures, the reduction of CO_2 to CO will disturb this mass balance and complicate the band analysis and the subsequent calculation of the corresponding surface pKs. However, it is still possible to gain this information under appropriate experimental conditions, i.e. adjusting the lower potential limit to avoid the reduction to CO by adsorbed hydrogen. In addition, assuming that the absorption coefficients are those determined for Pt(111), the corresponding surface pKs can be estimated.

In this study the stepped surfaces vicinal to the Pt(111) pole have been examined. As shown in the figure below, for the Pt(110) limiting case, the surface pK_2 is lower than that of Pt(111), at the corresponding potentials of zero free charge. This means that the more open surface behaves as being more alkaline than the closest packed one and thus adsorbed bicarbonate dissociates more easily to adsorbed carbonate.

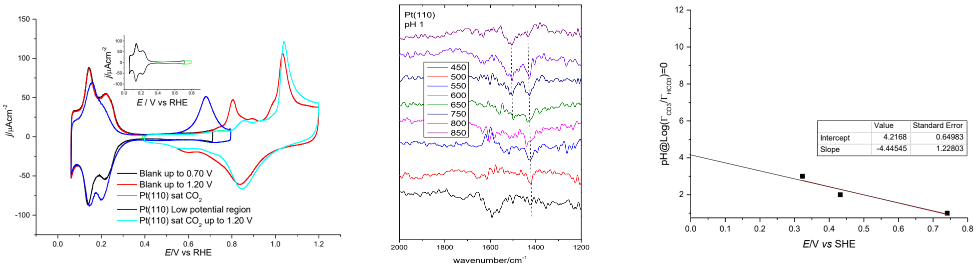

Figure. From left to right: voltammetry of Pt(110) in 0.1 M perchloric acid saturated with CO_2; spectra form this solution taken at different potentials: the bicarbonate band is observed (≈1400 cm^{-1}) and the carbonate band appears later (≈1500 cm^{-1}); plot of the surface pK_2 values at different potentials.

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Electrodeposition of Zn-Mn/Al_2O_3 Composite Coatings

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Zinc and zinc alloy coatings containing micro- and nano-Al_2O_3 particles offer a wide range of potential applications in various fields, due to promising economic benefits and their excellent properties such as wear and corrosion resistance [1]. Despite several reports that deal with plating of Zn-Ni composites containing Al_2O_3 particles, the electrodeposition of Zn-Mn-Al_2O_3 composite has not been reported yet. This type of coating could offer excellent corrosion protection, because the Zn-Mn alloy has been known to show the highest corrosion resistance among all Zn alloys, in chloride rich environment [2].

In this study, co-deposition of Zn, Mn, and Al_2O_3 particles via electrodeposition method was studied. Composite coatings were produced on steel substrate, using different deposition parameters such as current density and metal ion content of the bath solution. The electrodeposition bath was the simple chloride electrolyte commonly used for Zn-Mn electrodeposition, consisting of KCl, H_3BO_3, $ZnCl_2$ and $MnCl_2$, with added Al_2O_3 powder. Microstructural properties of the coatings were characterized by scanning electron microscopy, while the chemical composition was measured with electron dispersive spectroscopy. The corrosion behavior of the coatings in 3.5 mass.% NaCl aqueous solution was evaluated by using Tafel extrapolating method (determination of corrosion potential and corrosion current density) and electrochemical impedance spectroscopy.

It was found that co-deposition of alumina particles with Zn and Mn metals was successfully achieved via electrodeposition method, without agglomeration of ceramic particles. The electrodeposition conditions that enable the formation of non-porous coatings, where Al_2O_3 particles are distributed homogenously, were determined. The analysis of the chemical composition showed that the Mn content was low, i.e. up to 1.0 wt.%, while the Al content ranged between 0.10 and 7.0 wt.%. The increase in deposition current density from 10 to 40 mA cm^{-2}, results in decrease in alumina content of the coatings.

The measured corrosion current densities of Zn-Mn/Al_2O_3 coatings vary between 4.5 and 13.5 $\mu A\ cm^{-2}$, which is the typical corrosion rate of Zn alloy coatings in chloride environment. No correlation between Al_2O_3 content and the corrosion performance of the coatings was found. Therefore it is concluded that the alumina particles may be incorporated in Zn-Mn alloy coating, in order to enhance its mechanical properties, and without deteriorating its corrosion behaviour.

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Electrochemical and mechanical study of electrodes used in solid-state lithium batteries: a combined experimental-modeling approach

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Lithium-ion batteries have become a key technology in our everyday lives, and great interest has grown during the past decade towards new materials and new configurations of the cells. Solid state lithium batteries (SSB) allow having higher energy density without compromising power and capacity, while assuring high safety at variable temperatures and good cycle stability. However, during the charge and discharge of these batteries, there are significant volume changes in the electrodes that produce stress and strain effects on the solid materials. These effects can make layers separate and cracks to form in the battery materials, which reduces the potentially improved performance of these batteries. Furthermore, these mechanical depredating effects are more several in cobalt-free materials (Ni-Mn-based oxide electrodes), which are an ethical alternative for materials in battery systems but present structural weakness that are subject of study.

Our main goal is to investigate structural stability of cobalt-free battery electrodes (LMO, LMNO) and to develop a tool that allows to determine under which operation conditions a solid-state battery can operate without suffering relevant mechanical stress. The approach used combines In-situ Spectroscopic Ellipsometry, AFM techniques and Finite Element Modelling. First results show evident degradation of the electrodes and thickness changes at different states of lithiation.

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Electrodeless Photo-assisted Etching of Gallium Nitride with Potassium Peroxomonosulfate Oxidants

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While GaN has been widely used in fields of electronics and optoelectronics, its super stabile characteristic makes conventional chemical wet-etching methods inefficient. The photoelectrochemical etching is the only efficient approach because the photogenerated holes can activate GaN. For fabricating the GaN-based devices, the current mass manufacturing technology is the electrodeless photo-assisted etching that uses Ti/Pt nanofilm as electrochemical cathode and photo-mask to prepare the GaN pattern. However, this technology is still unable to prepare the flat and smooth GaN surfaces so far [1]. To improve this technology, we employed KSO_5 as oxidants. The electrochemical and photochemical responses of KSO_5 on Pt, Ru, and glassy carbon electrode were systematically investigated. Experimental results indicate that KSO_5 has a higher oxidation potential than $K_2S_2O_8$. The latter is the most frequently used oxidant in the currently electrodeless photo-assisted etching technology [2]. The use of KSO_5 enables the photoelectrochemical etching of GaN at a high potential. Thus, the roughening effect of electron-hole recombination, which preferentially occurs at dislocations in GaN film, can be avoided. However, it was found that a slight change in the pH of the GaN surface might cause a remarkable difference in the etching rate, which would lead to a rough GaN surface as well. To keep the pH of the whole GaN surface consistent during the etching process, a spin-etching method was developed. Results show that a flat and smooth GaN surface with a surface roughness Ra of 6 nm can be prepared at an etching rate of 18 nm/min.

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Development of continuous processes for the Electrochemical Reduction of CO_2 to Formate: evolution with electrodes of different nature and configuration

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The historic Paris Agreement on Climate Change, which aims at holding global temperature rise to well below 2ºC, represents a call for further action and for investment towards a low carbon, resilient and sustainable future. In order to mitigate excess anthropogenic carbon dioxide (CO_2) emissions (approx. 4GtC yr^{-1}) and achieve the 2ºC target, a portfolio of strategies and technologies need to be implemented together, where Carbon Capture Utilisation and Storage (CCUS) can play an important role. The utilization of captured CO_2 as a useful raw material, and particularly, the electrochemical conversion of CO_2 into products with value added has gained renewed and increasing attention over the last years [1-2]. Formate, or formic acid depending on pH, is a product of great interest, because, apart from its industrial applications, it is currently considered as one of the most promising compounds for hydrogen storage and as a promising candidate fuel to be used in fuel cells.

This lecture will summarise some of the results obtained by the DePRO research group of the University of Cantabria on the development of continuous processes for CO_2 electroreduction to formate in a flow reactor, with a single pass of the reactants through the reactor, in which the performance has been progressively improved by using electrodes not just of different nature (Pb, Sn, Bi), but also of different configurations: e.g. plate electrodes, particulate electrodes made of nanoparticles deposited on porous supports, or “Gas Diffusion Electrodes” (GDEs). Special attention will also be paid to discuss the results obtained with the configuration of “Catalyst Coated Membrane Electrodes” (CCMEs), in which catalyst nanoparticles are directly sprayed over a Nafion membrane. The CCME configuration allows avoiding the use of a liquid catholyte, so that the input feed to the reactor is simply a mixture of CO_2 and vapour, making it possible to achieve higher formate concentration (of up to 26 $g \cdot L^{-1}$) with an energy consumption 50% lower than using the same catalysts in GDE configuration.

The results obtained so far are promising and they suggest a great future potential of these approaches. However, much more research is needed to overcome the current limitations of these processes so that they are able to combine, simultaneously, high Faradaic efficiency, high rates of formation of the product (measured by the current density at which the process can be operated), high concentration of the product obtained (to avoid the economic and environmental penalty of subsequent purification), and low overpotentials to allow an energy efficient process, necessary to explore their scale-up.

Acknowledgements
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Corrosion of Zn-Ni coated reinforcing steel in simulated concrete pore solutions

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Zinc coating produced by the hot-dip galvanizing process is often used as a preventive corrosion measure in reinforced concrete structures exposed to carbonation or mild contamination with chlorides, because Zn forms a passive film of sufficient thickness [1]. However, during a prolonged exposure to the chloride-rich environment after the concrete carbonation, galvanized steel quickly corrodes once the threshold concentration of chloride ions is reached. Alloying with Ni is a common technique employed to increase Zn protective properties and hardness, and the market for corrosion resistant Zn–Ni coatings is large, primarily including coatings for automobile steel bodies and electronics industry. With this background knowledge, the present work is intended to study whether an electroplated Zn-Ni coating of a sufficient thickness may provide better long-term corrosion resistance to the reinforcing steel in concrete, in comparison to pure Zn coating. The Zn-Ni coatings were 40 μm thick and contained ~13 mass.% Ni.

There is no single electrolyte which may be used in a laboratory to simulate universal conditions in concrete, because in real concrete, many factors change with time, such as pH value and the concentration of corrosive species. Yet, based on previous studies [2], our work uses three different simulating electrolytes, to predict and compare Zn and Zn-Ni behavior in three environments: fresh concrete, concrete with CO_2 absorbed, and finally concrete with Cl^- ions. In order to compare their corrosion behavior, the pure Zn and Zn–Ni alloy coated steel samples were successively exposed to three different solutions. In corrosion testing, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) were used.

Impedance spectroscopy showed that both Zn and Zn-Ni were passivated in an alkaline solution (simulating fresh concrete) and carbonated solution, which simulated CO_2 ingress into concrete, but in the third, i.e. chloride rich solution, the deterioration of the passive layer on top of the coatings occurred, as expected. Nevertheless, the corrosion pattern is quite different for the two coatings: Zn–Ni surface was flat and black during the total immersion period in chloride solution, while Zn was covered with a white, chloride rich product that was constantly increasing in volume and peeling off the sample. The EIS measurements show significantly slower dissolution of Zn-Ni coating in the chloride environment, as compared to Zn. Therefore, it may be concluded that Zn-Ni could be a reasonable alternative to pure Zn for the protection of steel in concrete where a high chloride penetration is expected.

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Gold Nanoparticles Functionalized with Calix[4]arenes as Selective Catalysts for Oxygen Reduction Reaction (ORR)

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In the race of new technologies keen to obtain new sources of low-cost and sustainable energy, activation of abundant small fuel molecules (such as O_2, H_2O, CO_2 and H_2) is now widely studied to convert their chemical energy into an electric one[1]. However, the multi-electronic processes commanding these activations are not yet fully understood and controlled, but they have been observed to be efficiently catalyzed in nature through the action of metalloenzymes, in which a catalytic site is buried inside an organized molecular environment governing the reactivity.

Herein, we propose a strategy inspired from metalloenzymes to control the interfacial reactivity at the molecular level. This approach is based on the functionalization of metallic nanoparticles through the reductive grafting of calix[4]arene-tetradiazonium salts. The gold nanoparticles is then chemically modified with a well-organized monolayer of calix[4]arenes that are covalently bound to the surface.[2] These grafted nanocavities mimick an organized molecular environment that is likely to impact the orientation and approach of O_2 while ensuring strong stability of the electrocatalysts, thanks to multiple anchoring. The various functional groups at the calix[4]arenes small rim will modulate the interactions at the interface between the metal surface and the electrolyte/reactants due to their different hydrophilic and oxophilic natures. Herein, we will present the synthesis and electrochemical properties of these systems along with very promising results for obtaining stable and selective catalytic system for oxygen reduction reaction (ORR).

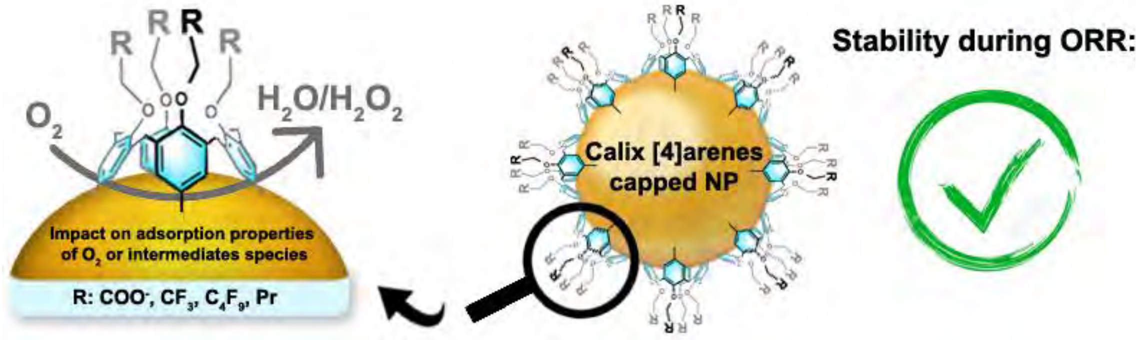

Figure 1. *Grafting of calix[4]arenes with various functional groups on gold NPs modifying O_2 adsorption phenomena and their influence on the ORR performances*

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Introducing Ionomer Nanofiber Scaffolding into the Cathode of Polymer Electrolyte Fuel Cells for Improving Robustness Against Humidity Changes

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For improving the power density of polymer electrolyte fuel cells (PEFCs), the transport resistances of the reactants (oxygen and proton) and product (H_2O) in the cathode catalyst layer (CL) need to be reduced. For simultaneously reducing these resistances, a CL containing a non-woven mat of ionomer nanofibers formed by electrospinning has been found to be promising owing to the presence of continuous proton pathways and pores [1]. The robustness of the cell performance against the humidity and optimal structure of the CL are, however, yet to be clarified. In the present study, we fabricated CLs with ionomer nanofiber scaffoldings (iNFS-CL) where the ionomer loading and distribution between the mat and Pt/C region were systematically changed, and the cell performances were analyzed on the basis of the elemental characteristics, including the mass transport properties (proton, water, oxygen) under different humidity conditions.

A scanning electron microscope (SEM) image of an iNFS-CL fabricated by one cycle of the electrospinning and electrospraying is shown in Fig. 1a, and indicates that Nafion nanofibers are uniformly covered with the catalyst particles. The cell performances with the gas supplies of H_2/air (21 kPa O_2) were evaluated at the cell temperature of 80 ºC in the humidity range of 30%RH - 165%RH. Figure 1b shows the current densities at 0.5 V (IR-corrected with high frequency resistances) for the iNFS-CLs with different overall ionomer/carbon weight ratios (I/C) with the local I/C of 0.4 in the Pt/C region and for conventional CLs (Conv.). The three iNFS-CLs (overall I/C = 0.8, 1.0, and 3.0) show higher current densities than Conv.-1.0 (I/C = 1.0) over the humidity range of 30%RH - 165%RH. The Conv.-0.8 (I/C = 0.8) shows comparable performances above 50%RH but inferior performances below 50%RH to the iNFS-CLs. The results indicate that iNFS-CLs have higher robustness against humidity changes than for conventional CLs. In the meeting, the results on analyses of their elemental characteristics will be presented and the origins of the higher robustness for the iNFS-CLs will be discussed.

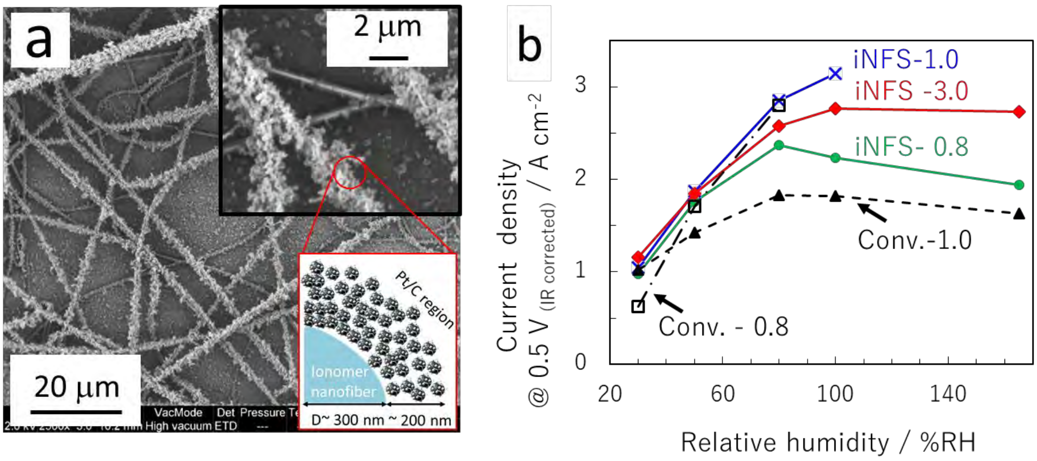

Figure 1 (a) SEM image of an iNFS-CL and schematic diagram of the cross-section of the ionomer nanofiber covered with the catalyst particles. (b) Humidity dependence of current density at 0.5 V (IR-corrected) of polarization curves in the anodic scan (10 mV s^{-1}).

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Atomically Dispersed Fe/N-Codoped Nanocarbon for Bifunctional Oxygen Electrocatalyst Synthesized by Self-Template and Polypyrrole Encapsulation Method

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High performance and durable bifunctional oxygen electrocatalysts are of great importance for the commercial application of environmentally friendly and sustainable energy through electrochemical devices such as rechargeable Zn–air batteries and fuel cells. Highly distributed catalysts with maximum atomic utilization are considered to be a promising alternative for current noble-metal-based catalysts. Herein, a high performance and durable bifunctional oxygen electrocatalyst for both ORR and OER is synthesized by a facile self-template and polypyrrole encapsulation method. The super performance AD-Fe/N-C-900 catalyst has a special open porous double shell hollow structure which is beneficial to exposure of more Fe-Nx active sites for ORR and OER, and improves mass transfer, resulting in a fabulous bifunctional ORR/OER electrocatalytic activity ($\triangle E$ =0.655 V), which is better than the commercial Pt/C ($\triangle E$ =1.035 V) and the commercial IrO_2 ($\triangle E$ =0.93 V), along with remark durability and long-term stability for the ORR in alkaline medium. Based on our results and analysis, the remarkable electrocatalytic activity of AD-Fe/N-C-900 might be attributed to the high content of mesopore, high density of Fe-Nx active sites, and robust double shell hollow structure. The novel design of the atomically dispersed Fe/N-codoped porous double shell hollow nanocarbon enable boosted oxygen catalyst by a facile method has certain enlightening effect on the design and development of other bifunctional electrocatalysts in the next generation reversible energy conversion systems. Our work provides a design idea for the synthesis of high activity and stability bifunctional atom-level distributed catalysts..

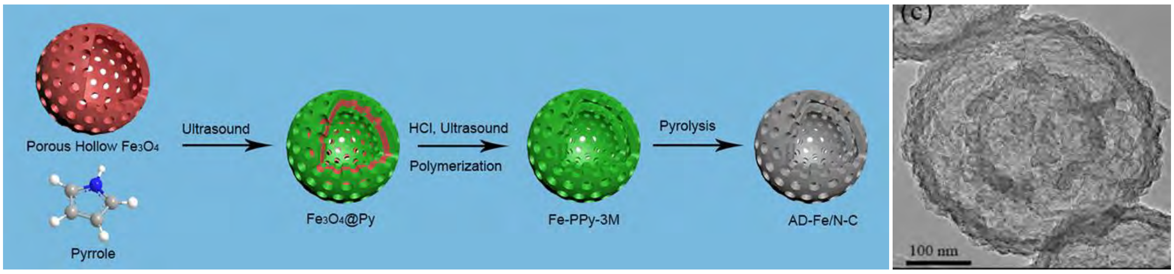

Figure 1. Synthetic route of AD-Fe/N-C catalyst.

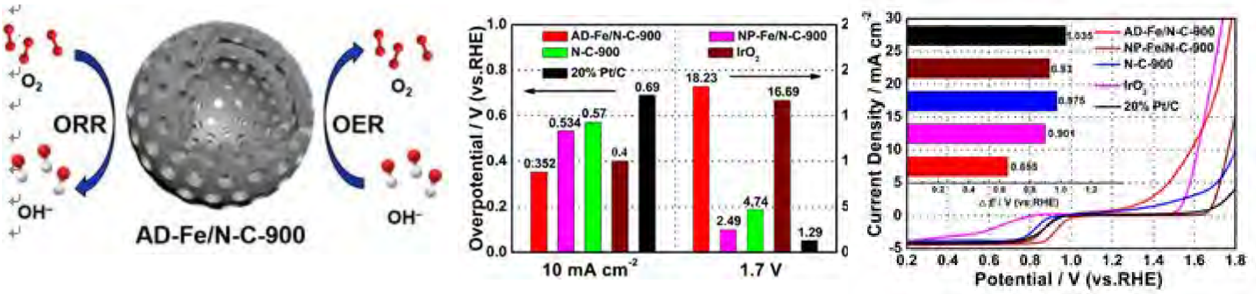

Figure 2. (a) Bifunctional Oxygen Electrocatalyst; (b) Bar plots of overpotential at the current density of 10 mA cm^{-2} and current density at 1.7 V of catalysts; (c) polarization curves of catalysts tested in the full OER/ORR region in O_2-saturated 0.1 M NaOH solution at a scan rate of 10 mV s-1 at 900 rpm

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The investigation of heterogeneous oxygen consumption on a single *Caenorhabditis elegans* animal by scanning electrochemical microscopy.

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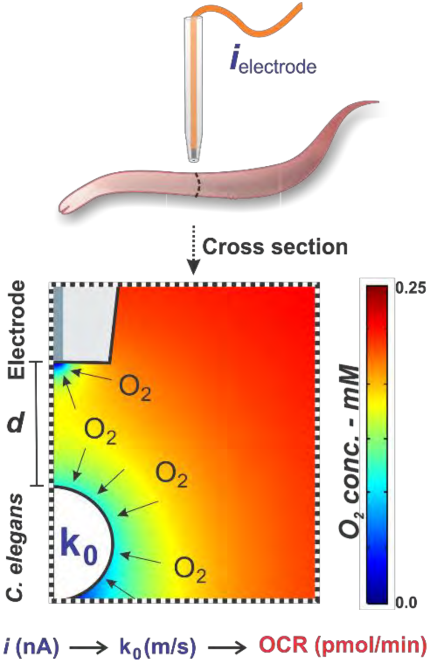

Scheme 1. Schematic representation of the experiment performed to determinate the local OCR in a single *C. elegans*.

Scanning electrochemical microscopy (SECM) was employed to investigate the respiration metabolism of the nematode *Caenorhabditis elegans*, an animal widely used as a model for aging and caloric restriction studies due to its metabolism, physiology, as well as easy handling and short-lifespan [1]. Drug effects and contribution of different diets on the animal's metabolism are commonly evaluated by accessing the respiration activity by measuring the oxygen concentration in a solution containing a large number of worms, as the oxidative phosphorylation is the last stage of the majority of metabolic processes. This is done by monitoring changes in the oxygen consumption rate (OCR), measured by commercial equipment (e.g.: Clark electrodes). The known advantages of SECM that allow gaining localized information by performing space-resolved electrochemical measurements were used here for investigating the local OCR at different parts of a single animal. A platinised platinum microelectrode working as an SECM tip in redox competition mode [2] (electrode/sensor and animal consumed the same species, oxygen) was employed as a tool for mapping the oxygen consumption at the vicinity of a single *C. elegans*. The local oxygen consumption rate (OCR) was determined by fitting a series of measurements performed in different regions of the animal to the calculated SECM tip response using Finite Element Method (FEM – COMSOL Multiphysics) (Scheme 1). The results indicated that the main contribution for the total oxygen consumption of the animal is the reproductive system (gonad) in the adult hermaphrodite *C. elegans*. For understanding the role of the reproductive system, we have compared the local OCRs in the wild (N2 Bristol) and mutant animals (glp-1), which has no development of the reproductive system. We also made use of fluorodeoxyuridine (FUdR) to interrupt egg development in the wild animal, allowing us to investigate the contribution of egg development in the reproductive system metabolism. This is the first time that such information is reported and may contribute to a better understanding of the animal's metabolism and help in the proper interpretation of bulk OCR measurements (large number of worms).

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Carbon-free Cathodes for Li-O_2 Batteries based on Transition Metal Oxynitrides-Nitrides

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Oxynitrides-nitrides of several transition metals were synthesized by sol-gel using alkoxides and chlorates. Interconnected porosity was incorporated through phase separation of hydrophilic and hydrophobic blocks, and elimination of organic components with a thermal treatment. Partial substitution of oxygen by nitrogen was accomplished using thermal treatment in NH_3 atmosphere and incorporation of urea during the synthesis procedure. Powder characterization includes surface area (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD) and cyclic voltammetry (CV). The results show surface areas higher than 150 m^2/g, and the catalytic activity depend on the combination of oxides, nitrides and oxynitrides.

Fabrication and Characterization of Electrospun PVAM/TEOS Based Gel Polymer Electrolyte

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Gel polymer electrolyte (GPE) is a promising alternative for the toxic and flammable liquid electrolyte in lithium ion batteries because of leak proof, longer shelf life and safety concerns. GPE consists of a porous polymer host and liquid electrolyte saturated within and combines the advantages of both the liquid and solid components [1].

In this study, a novel three-dimensional network GPE based on poly(vinyl alcohol)/maleic anhydride/tetraethyl orthosilicate (PVA/MA/TEOS) with polymer fibers were developed. Crosslinked nanofibrous polymer membranes for GPE of various composition were fabricated by UV-electrospinning method. The dual crosslink polymer membranes were obtained after heat treatment of as-prepared polymer nanofibers, due to the condensation of hydrolyzed TEOS. The morphology of the electrospun membranes was studied using scanning electron microscopy as shown in Figure 1. The uniform and well cross-linked nanofibers were formed with addition of 5 and 10% of TEOS.

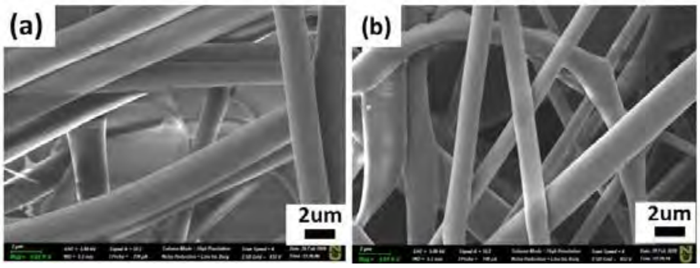

Figure 1. SEM image of PVA/MA/TEOS fibers with (a) 5% and (b) 10% TEOS

The excellent thermal properties of the membranes were proven using thermal gravimetric analysis. The membranes have an improved porosity and exhibit high uptake when activated with the liquid electrolyte of lithium salt in a mixture of organic solvents, and also show high liquid retention properties. Electrochemical impedance spectroscopy and linear sweep voltammetry testes showed a high conductivity and vide range (up to 5.5 V) electrochemical stability of prepared GPE. Electrochemical performance of the polymer gel electrolyte is evaluated in Li/polymer electrolyte/$LiFePO_4$ coin cell with various current density and showed promising results.

Acknowledgements

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Capacity limiting effects for freestanding, monolithic TiO_2 nanotube electrodes with high mass loadings

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TiO_2 nanostructures have been extensively studied as alternative electrode material for lithium-ion batteries specifically for applications where high power is needed [1]. The high operation potential, 1.8 V, makes TiO_2 a safer alternative compared to graphite but also increases the demand for positive electrode materials with high potentials to yield a battery with a descent cell voltage [1]. The theoretical capacity of TiO_2 is 335 mAh/g but in practice lithiation degrees corresponding to around $Li_{0.5}TiO_2$ are reported [2,3]. The electrical conductivity of TiO_2 is comparably low and this has been reported as a problem for bulk electrode materials, although nanostructuring of the electrode materials can be used to decrease this problem significantly. TiO_2 nanotubes can be synthesized in a two-step anodization process with a fluoride containing electrolyte resulting in freestanding TiO_2 nanotubes on a titanium substrate [4].

In the present work, the capacity limiting factors are studied for TiO_2 nanotubes with mass loadings up to 10.5 mg/cm^2, corresponding to tube lengths from 4.5 µm to 40.5 µm. The results show that higher capacities are obtained for cyclic voltammetry compared to galvanostatic cycling. A diffusion controlled decrease in capacity is seen for the nanotube electrodes as the cycling rate is increased and a maximum average lithiation degree corresponding $Li_{0.55}TiO_2$ is obtained. This effect stems from the decrease in the diffusion rate as the concentration of Li_xTiO_2 increases in the electrode. The results also indicate the presence of a lithium-ion trapping in the electrode during cycling with a similar behavior as that previously seen [5] for lithium-alloy forming electrode materials.

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Activity Enhancement of thin-film Pd catalysts by Bi adatoms towards alcohol electrooxidation in alkaline media

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Thin-film Pd catalysts with low metal loadings (55 and 110 µg cm^{-2}) were obtained by electrodeposition on CG electrode from a surfactant-free green electrolyte. Surface of Pd electrode was modified by irreversibly adsorbed Bi as fast and easy to do method. The catalysts were characterized by AFM technique and demonstrated that the nanoparticle clusters was formed from the agglomeration of single crystal particles. The catalytic activity and durability of Bi-modified Pd electrodes on methanol and ethanol electro-oxidation in alkaline media was investigated. The participating roles of Pd and Bi was examined from the aspect of different Pd metal loadings and Bi surface coverages. The presented electrochemical tests shown that the modification with the appropriate amount of Bi on thin-film Pd catalysts enhance activity toward MOR and EOR up to about 2-3 times compared to unmodified catalysts. Besides surface Bi coverage (Θ_{Bi}) of 0.6 increase durability and provides more poisoning tolerant Pd/GC electrode in both studied reactions as it is presented in Fig. 1.

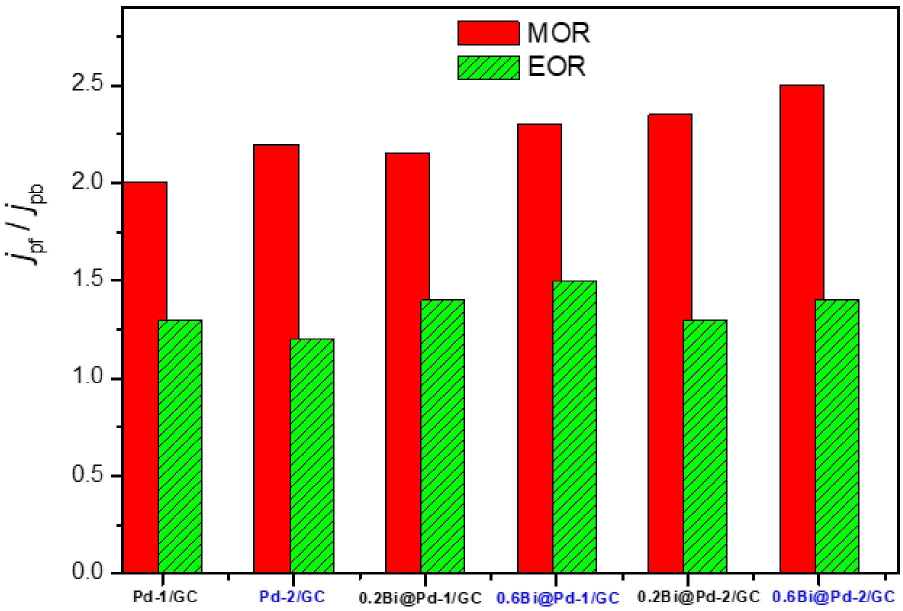

Fig. 1 The ratio of the forward peak current density (j_{pf}) and the backward peak current density (j_{pb}), as the parameter of the poisoning tolerance to the carbonaceous species for Pd catalysts in methanol and ethanol oxidation reaction in alkaline media.

It was concluded that the combination of third body and bifunctional effect is responsible for the electrocatalytic improvement of thin-film Pd catalysts modified with Bi in examined reactions of alcohol oxidation in alkaline media. Electrochemical investigations of such modified electrodes signify how to direct research in order to develop an efficient catalyst.

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Creating Precise Dual-molecule Junctions to Probe Intermolecular Crosstalk

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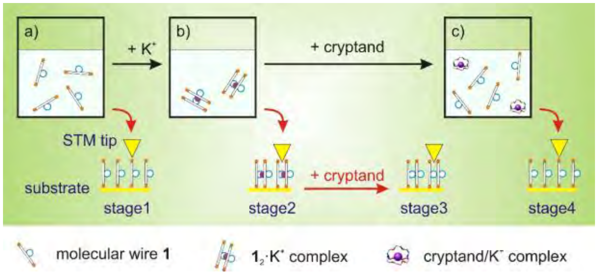
Understanding and controlling charge transport across multiple parallel molecules is fundamental to the creation of innovative functional electronic components,[1] as future molecular devices will likely be multi-molecular.[2] The smallest possible molecular ensemble to address this challenge is a dual-molecule junction device, which has potential to unravel the effects of intermolecular crosstalk on electronic transport at the molecular level that cannot be elucidated using either conventional single-molecule or self-assembled monolayer (SAM) techniques. Herein, we demonstrate the successful fabrication of an STM dual-molecule junction device, which utilizes noncovalent interactions and allows for direct comparison to the conventional STM single-molecule device. STM-BJ measurements reveal a decrease in conductance of 10% per molecule from the dual-molecule to the single-molecule junction device. Quantum transport simulations confirm this decrease is attributable to direct intermolecular crosstalk (i.e. intermolecular π-π interactions), with contributions from substrate-mediated coupling (i.e. molecule-electrode). This study provides the first experimental evidence to interpret intermolecular crosstalk in electronic transport at the STM-BJ level, and translates the experimental observations into meaningful molecular information to enhance our fundamental knowledge of this subject matter. This approach is pertinent to the design and development of future multi-molecular electronic components, and also to other dual-molecular systems where such crosstalk is mediated by various noncovalent intermolecular interactions (e.g. electrostatic and hydrogen bonding).



Scheme 1. Schematic steps to construct the dual-molecule STM-BJ junction device.

Figure 1. Single-molecule (left), supramolecular (middle), and dual-molecule (right) junction devices comprising 15-crown-5 derivatized oligo(phenyleneethynylene) (OPE) wire **1**, and their measured conductance values.

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Surfactant addition to the electrolyte solution to increase capacitance of metal oxide-based supercapacitor electrodes

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Electrode materials employed in supercapacitor electrodes are always highly porous with large specific surface area residing inside pores of the material. This applies in particular to carbon-based materials used in currently commercially available electrochemical double layer capacitors (EDLC), it is also true for redox active materials (e.g. metal oxides [1], mixed metal oxides [2], intrinsically conducting polymers or composites of these materials [3]). With increasing porosity yielding the requested large surface area needed for charge storage in particular with EDLC the challenge of complete utilization of the surface area as measured e.g. with porosimetry or BET-method as contact area between the electronically conducting electrode material and the ionically conducting electrolyte solution grows. In addition some of the surface of these materials might not be as hydrophilic as would be preferable for complete wetting.
Addition of surfactants (non-ionic, cationic as well as anionic [4]) has been suggested and examined mostly with carbon-based materials [5]. We have examined this concept with a representative metal hydroxide $Ni(OH)_2$ and a mixed metal oxide $MgCo_2O_4$ electrode material.

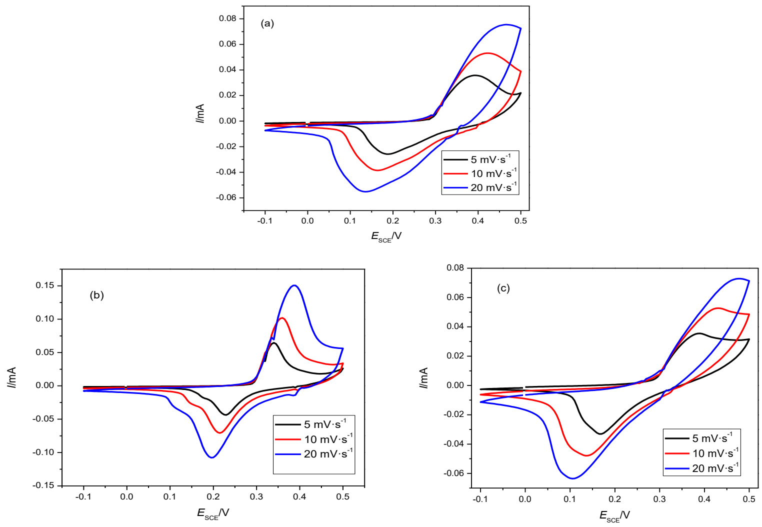

Fig. 1: CVs of (a) the as-prepared "α-$Ni(OH)_2$"-coated electrode in an aqueous solution of 1.0 **M** KOH; (b) with added 10 **µM** Triton X-100; (c) with added 10 **µM** SDS.

Addition of the non-ionic surfactant Triton X-100 resulted in a significant increase of peak current density, peak separation decreased in addition indicating enhanced electrode kinetics. With anionic SDS the effects were less pronounced. Galvanostatic charge-discharge measurements confirmed these observations, they also showed higher capacitance retention with increasing current density. Within the limited timespan of our preliminary experiments, stability of the performance was improved by surfactant addition. Coulombic efficiency closely related to self-discharge was improved with SDS addition, with Triton X-100 efficiency was poorer at low current densities. The mixed metal oxide did not show any improvement, possibly related to surface reactions of this material elsewhere used in heterogeneous catalysis with the added surfactants.

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Organic Polymers as Electrodes for Structural Energy Storage

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Volume and/or weight savings in mobile devices, electric/hybrid ground transport and aircraft are critical design drivers. One approach to improve the system level specific energy is by adding electrical energy storing capability to structural components, making multifunctional materials.[1,2] However, commercialized batteries and supercapacitors, traditional energy storage devices, are typically rigid and heavy due to the currently used fabrication techniques based on the slurry-casting method and traditional configuration.[3]

The application of organic redox-active polymers as electrode materials has attracted remarkable attention owing to their flexibility, low cost, recyclability, fast response ($<10^{1-3}$ s), capacity ($>10^2$ mAh g^{-1}), and capability for tuning the redox potential.[4] In this study, we hybridize two aromatic carbonyl derivative polymers with carbon-based materials to improve the efficiency of energy storage devices by compensating for the low polymer conductivity, contributing electrical double-layer capacitance, and improving the mechanical properties of the electrodes. These materials are discussed in terms of their physico-chemical, mechanical and electrochemical properties (Figure 1), before being used as electrodes in aqueous batteries. The aqueous electrolyte provides greater safety, much lower cost, higher power density, and much faster recharge rate due to more efficient ion transport. The hybrid cathode provides 4 times higher gravimetric capacity than the unmodified carbon-based material.

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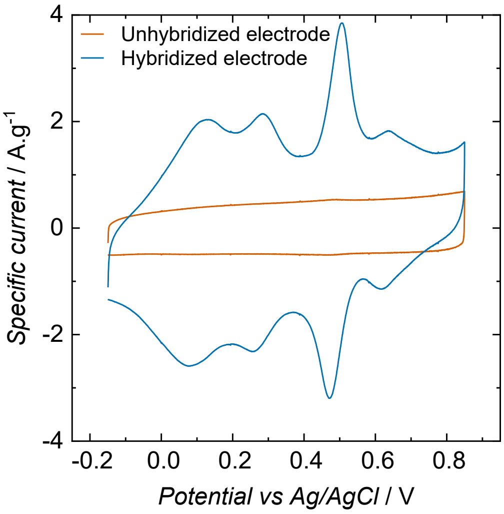

Figure 1: Voltammetry (10 mV s^{-1}) in 1 M H_2SO_4 of single-walled carbon nanotube bucky paper before and after hybridization with an aromatic carbonyl derivative polymer.

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In-situ XAS Investigation of the Copper Oxidation State During the Electrochemical Conversion of CO_2 on Nanostructured Copper Titanates

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The impacts of climate change and global warming have become a topical subject in both the political and scientific landscapes in recent times. The significant increase of anthropogenic carbon dioxide (CO_2) in the atmosphere through the widespread use of fossil fuels to produce energy to meet the ever-increasing global demand and consumption of energy is of great concern. The capture and recycling of atmospheric CO_2 is a promising pathway to address this global challenge. In particular, the electrochemical conversion of CO_2 to useful, value-added chemicals is the subject of significant research effort because this avenue affords an opportunity to take advantage of electrical energy generated by renewable sources such as wind, water and solar.

The specific chemical and physical properties of the CO_2 reduction reaction (CO_2RR) catalyst plays a significant role in the catalytic process. Elemental composition, surface geometry, oxidation state, particle size and morphology impact the selectivity and efficiency of CO_2RR.[1,2,3] Copper and copper oxide-derived surfaces are the only catalysts that can electrochemically convert CO_2 to high value and energy-dense C2 and C3 products.[2,4]

Herein, we present time-resolved *in-situ* XAS monitoring of the Cu oxidation state during CO_2RR in a neutral aqueous media for a series of Cu-titanate nanoparticles. Electrochemical characterization combined with On-line Electrochemical Mass Spectrometry (OLEMS) provides insight into the impact of Cu oxidation state on product selectivity.

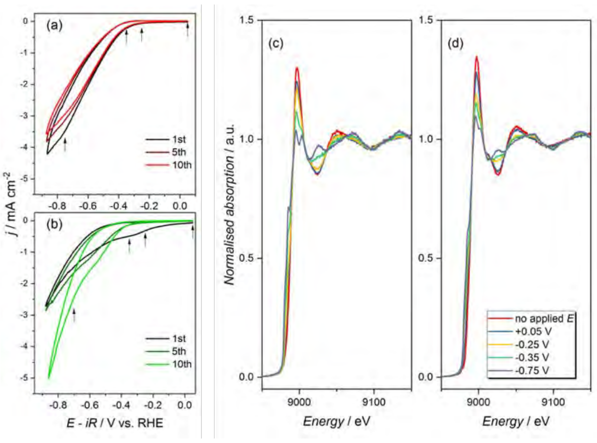

Figure 1. (a) 9 wt.% Cu:NTO and (b) 10 wt.% CuO@NTO catalysts in CO_2-saturated 0.1 M K_2HPO_4 / KH_2PO_4 buffer solution (pH 6.5) utilising a RDE; ν = 50 mV s^{-1}; rotation = 1200 rpm. The annotated arrows indicate the potentials applied during *in-situ* XAS measurements. Normalised *in-situ* Cu K-edge XANES spectra of (c) 9 wt.% Cu:NTO and (d) 10 wt.% CuO@NTO recorded in CO_2-saturated 0.1 M K_2HPO_4 / KH_2PO_4 buffer (pH 6.5) at various applied potentials.

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p- and e- type Silver functionalized Dense Titanium Dioxide Semiconductor Layer for Efficient Perovskite photovoltaics (SOLAR)

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Perovskite solar cells (PSC) have an advantage over conventional silicon solar cells in its simplicity of processing and notable power conversion efficiency (PCE) of ~ 22%. However, their performance is limited by the recombination of charge carriers occurring at the TiO_2/PSC interface[1]. This work controls recombination at the Electron transport layer (ETL) (c-TiO_2+mp-TiO_2)/Perovskite interface through elimination of pinhole defects followed by Silver- functionalization (dense-TiO_2/mesoporous-Ag-TiO_2) to enhance the electrochemical surface and photo-absorptivity. An innovative method was used to construct a compact Ag functionalized a-TiO_2 film consisting of a mixture of ethanol, titanium(IV) isopropoxide, and silver nitrate spin coated on a fluorine-doped tin-oxide substrate in the absence of ZnO as supportive photoanode[2]. The performance of PSC/Ag–TiO_2 and TiO_2 films were probed using scanning electron microscopy (HRSEM), x-ray diffraction (XRD), UV-visible spectroscopy, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The uniformly distributed Ag-nanoparticles attached to the mesoporous TiO_2 matrix fashioned a TiO_2 compact layer with excellent blocking capability and improved electron mobility as observed in Fig.1. Particular Ag doping percentage of ~ 0.9% altered the electrical conductivity of the TiO_2 film, reducing the recombination process occurring at the ETL/PSC interface [3]. From IV-measurements, the PSC developed via two steps, yielded satisfactory effiencies. The dense-TiO_2/mesoporous-Ag-TiO_2 UV-Vis results revealed an induced red shift and band gap of 3.29 eV; indicative of enhanced luminescent properties. Hence, the synergy of dense TiO_2 and the surface plasmon resonance effect of metallic Ag nanoparticles successfully enhanced the optical absorption in the visible light region as well the power conversion efficiency compared to the pristine TiO_2 perovskite solar cell.

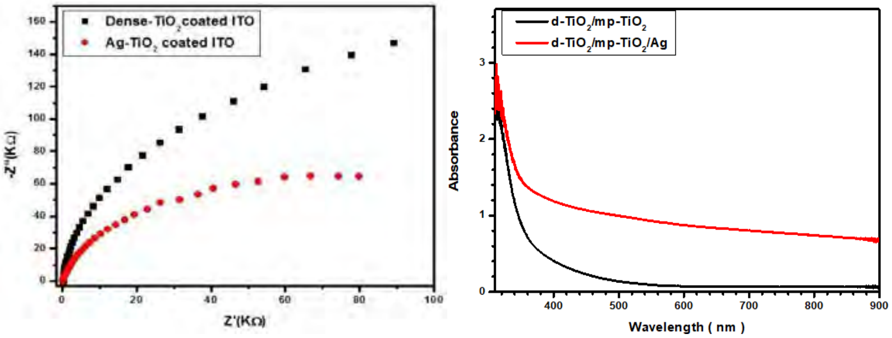

Fig.1. Electrochemical Impedance Spectroscopy and UV-Absorbance spectra of dense-TiO_2/mesoporous-Ag-TiO_2

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Nickel Hydroxide Anodes for Decoupled Water Splitting in an Electrochemical – Chemical Cycle

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As the human population grows, a transition towards clean and renewable energy sources becomes critical in curbing the negative effects of fossil fuel combustion. To facilitate this transition, renewable sources must be combined with energy storage and transportation infrastructures.

Hydrogen production by water splitting has long been considered a promising solution to mitigating the intermittency issues of renewable energy, while also providing a high energy fuel for transportation. However, water splitting technologies still face challenges to improve their performance, efficiency, and cost, especially when combined with renewable power sources [1]. In conventional electrolyzer technologies, hydrogen and oxygen are evolved simultaneously in the same cell, and a membrane or diaphragm is essential for product separation (Figure 1a). Nevertheless, dangerous H_2/O_2 mixtures may still form under partial load conditions, which are inherent to renewable power source. Such H_2/O_2 mixtures lead to accelerated membrane degradation, in addition to posing a safety hazard. Furthermore, the four-electron oxygen evolution reaction (OER) that takes place at the anode requires large overpotentials of over 400 mV, resulting in significant energy efficiency losses.

In this work, we present a strategy for high-efficiency decoupled water splitting, wherein hydrogen and oxygen are produced in two separate steps in an electrochemical – thermally-activated chemical (E-TAC) cycle [2]. The conventional OER catalyst anode is replaced by a cobalt-doped nickel hydroxide [$Ni(OH)_2$] anode; in the first step, hydrogen is produced at the cathode while the anode is oxidized to nickel oxyhydroxide [NiOOH] in an efficient one-electron reaction, having a significantly lower overpotential compared to the OER (Figure 1b, left). In the second step, the oxidized NiOOH anode is disconnected from the electrical circuit and heated, inducing its spontaneous chemical reduction reaction, which restores its initial composition while oxidizing water and releasing oxygen (Figure 1b, right). This E-TAC process enables hydrogen production at low voltages in a simple, cyclic process with high efficiency, robustness, safety, and scale-up potential.

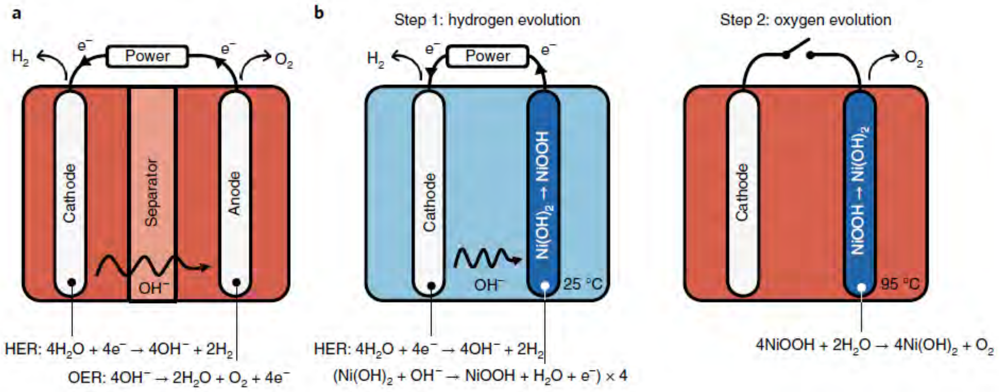

Figure 1: Schematic of alkaline water electrolysis (a) and the E-TAC water splitting process (b).

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Preparation of $ZnSe/MoO_3$ Co-modified TiO_2 Nanotube Composite Film for Photoelectrochemical Cathodic Protection

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TiO_2 semiconductors can provide photoelectrochemical cathodic protection for metals due to their special photoelectrochemical properties. However, pure TiO_2 semiconductors cannot sustain photoelectrochemical cathodic protection in the dark, which may limit their practical applications. Therefore, in this work we fabricated a $ZnSe/MoO_3$ co-modified TiO_2 nanotube composite film with charge storage ability and investigated its photoelectrochemical cathodic protection effect on 403 stainless steel.

A TiO_2 nanotube array film was prepared on a Ti foil in a two-electrode cell by anodic oxidation, then MoO_3 and ZnSe particles were deposited onto the film by cyclic voltammetry and pulse electrodeposition, respectively. Finally, a $ZnSe/MoO_3/TiO_2$ nanotube composite film with a cascade band structure was fabricated. The prepared films were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-Vis spectroscopy, and photoluminescence measurements. The photoelectrochemical cathodic protection effects of the prepared films were investigated by photoelectrochemical measurements.

The results showed that the TiO_2 film consisted of ordered nanotubes with an average inner diameter of about 100 nm and wall thickness of about 15 nm. This nanotube structure remained intact after MoO_3 and ZnSe particle deposition on the film. EDS, XRD, and XPS analyses indicated that the prepared nanotube composite film was composed of ZnSe, MoO_3 and TiO_2. The photoresponse of the $ZnSe/MoO_3/TiO_2$ composite film was extended to the visible light region, and the photo-induced electron-hole pair recombination was reduced. The photocurrent intensity of the composite film in a 0.5 M KOH solution was two-fold higher than that of the pure TiO_2 film. Under white light illumination, the $ZnSe/MoO_3/TiO_2$ composite film as a photoanode decreased the potential of the coupled 403 stainless steel in a 0.5 M NaCl solution by 470 mV relative to its corrosion potential, showing an effective photoelectrochemical cathodic protection effect. After the illumination was stopped, the composite film could continuously provide cathodic protection for 22.5 h resulting from its charge storage capability. The electrochemical impedance spectroscopy results also indicated that the composite film had the photoelectrochemical cathodic protection effect on 403 stainless steel.

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Electrochemical Deposition of Tin from Deep Eutectic Solvents

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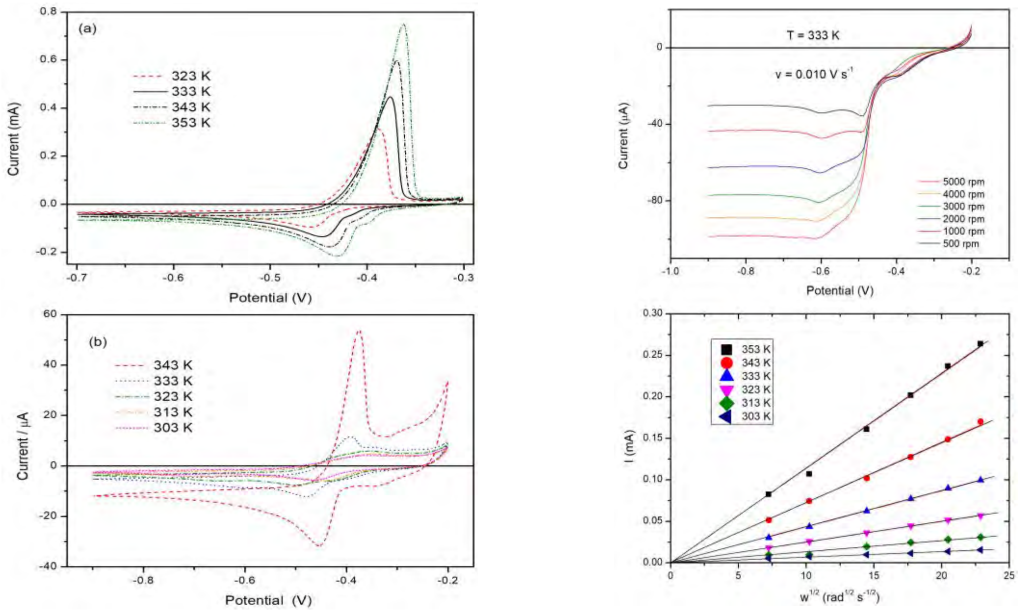
The electrodeposition of Sn from deep eutectic solvents (DES) on copper substrates was studied in the temperature range 303 -- 353 K using the mixtures of choline chloride with either ethylene glycol (ethaline) or urea (reline) in the ratio 1:2. For the characterisation of the electrochemical process, voltammograms were run between -0.25 and -1.0 V (vs. Ag wire quasireversible reference electrode). For both DES, the negative-going potential scans show first an underpotential deposition process, which is immediately followed by an overpotential electrodeposition process. The former is, however, considerably less distinguishable in DES compared with that obtained in aqueous acid solutions. Some significant differences were observed between the voltammetric profiles recorded in ethaline and reline. First, the current densities are much lower in reline, at all temperatures, probably related to the much higher viscosity and much lower conductivity of reline. Secondly, in ethaline the voltammogram presents a main single cathodic current peak while in reline, depending on the temperature, two or three electroreduction current peaks can be recorded. By means of a rotating disc electrode, Levich plots were obtained from which the diffusion coefficient of Sn(II) ions was determined at different temperatures within the studied range. Moreover, while a limiting current plateau is recorded bellow -0.4 V during the electrodeposition of tin from etaline, in reline the limiting current is preceded by a series of three small cathodic peaks. From the corresponding Arrhenius plots, the activation energy for the diffusion process was determined and compared to data from acid aqueous solutions. Both, voltammetric and chronoamperometric measurements provided evidence of a nucleation and growth process. Non-dimensional plots derived from chronoamperometric experiments at different electroreduction potentials were consistent with the occurence of a 3D instantaneous nucleation and growth process under diffusion control during the overpotential deposition. Impedance data recorded between 60kHz and 10 mHz showed the presence of two capacitive time constants in the potential range related to the underpotential deposition process and a single capacitive time constant at potentials related to the overpotential electrodeposition of Sn ions. SEM images obtained for the deposits formed in both DES show the presence of different morphologies according to both, the nature of the electrolyte and the electrodeposition routine employed.



Left: Voltammograms recorded at 0.01 V s^{-1} for a Cu electrode in ethaline (a) and reline(b) + 0.01 M $SnSO_4$ at different temperatures. Right: RDE linear sweeps obtained at 333 K in reline at different rotation speeds and the corresponding Levich plots.

Exciton Dynamics of Conjugated Polymer Films Studied by *in situ* Fluorescence Spectroscopy

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The operation of most organic optoelectronic devices based on conjugated polymers, namely organic light-emitting diodes, organic photovoltaic cells or luminescent electrochemical cells is determined by the interaction of photoexcited states (i.e. excitons) and charged species (i.e. polarons) of polymer films.

The measurement of exciton diffusion is a key aspect to design efficient devices. This is usually performed by means of spectroscopic techniques, which measure the efficiency of radiated photons in the presence of quenchers. The photoluminescence (PL) of thin films is usually measured in the absence and in the presence of a quenching site and the exciton diffusion length is derived from the PL quotient. In these studies, a statistically significant number of experiments are required to obtain consistent results and therefore many samples must be prepared. Electrochemical methods allow a reversible and controlled charge injection in conjugated polymers, leading to the formation of charged states, such as polarons which serve as quenching sites for excitons. The use of electrochemical instrumentation allows fine and precise control of the quencher concentration, thus permitting a simultaneous analysis of exciton dynamics within a single sample of conjugated polymer. The electrochemical *in situ* fluorescence spectroscopy (also known as electrofluorochromism) is a relatively novel tool that has been applied to the characterization of luminescent molecular systems and to the development of novel optoelectronic devices[1,2]. In the present work, a combination of electrochemical *in situ* steady-state fluorescence spectroscopy and UV-vis spectroscopy has been employed for the first time to determine the diffusion coefficient of excitons. The material selected for this study is MEH-PPV, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], an orange-red emitter widely employed in OLEDs and bulk heterojunction photovoltaic cells. In these systems, an annihilation process can occur when a photogenerated singlet exciton (S_1) finds a quencher (p):

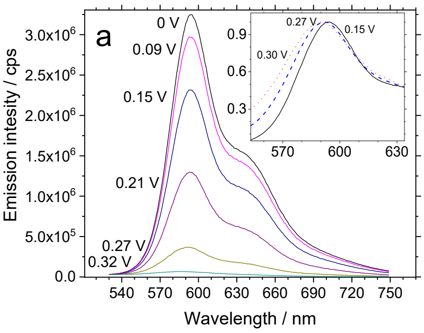

Figure 1: Evolution of the PL emission spectrum during the p-doping of a MEH-PPV film (λ_{exc}= 500 nm)

$$S_1 + p \overset{k_q}{\rightarrow} S_0 + p + phonons$$

being k_q the annihilation polaron-exciton rate constant. This bimolecular process competes with the monomolecular intrinsic de-excitation of excitons. The quenching process observed upon electrochemical doping (figure 1) follows a Stern-Volmer mechanism at low doping levels, with a time-independent rate constant typical of diffusion-controlled annihilation processes [3]. From both the Stern-Volmer rate constant and the exciton-polaron critical distance, an exciton diffusion coefficient can be derived [4]. These results support the suitability of spectroelectrochemical techniques as fast and powerful alternative tools for the reliable determination of exciton diffusion coefficients in conjugated polymers.

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On the Electrochemical Exfoliation of Graphite to Graphene

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Shortly after the birth of graphene, electrochemical exfoliation has been adopted to prepare graphene from various raw materials of graphite. In general, there are mainly three processes, ion intercalation/deintercalation, surface tailoring and bubbling dispersion, during the electrochemical exfoliation of grahite. We propose programed potential modulation strategies to balance these processes and obtained high-quality graphene with high crystallinity, low oxidation degree, uniform size distribution and few layers.

Another important issue is to functionalize the graphene simultaneously in the electrochemical exfoliation of graphite. GO plays important roles in the sustainable development of energy and the environment, taking the advantages of oxygen-containing functional groups for good dispersibility and assembly. Compared with Hummers' method, electrochemical exfoliation of graphite is considered facile and green, although the oxidation is pretty low. To synthesize GO with better crystallinity and higher oxidation degree, we present a photo-synergetic electrochemical method. By using oxalate anions as the intercalation ions and coreactant, the interfacial concentration of hydroxyl radicals generated during electrochemical exfoliation was promoted, and the oxidation degree was comparable with that of GO prepared by Hummers' method. In addition, the crystallinity was improved with fewer layers and larger size. Moreover, the aniline co-assembled GO membrane was selectively permeable to water molecules by the hydrogen-bond interaction, but it was impermeable to Na^+, K^+ and Mg^{2+}, due to the electrostatic interactions. Thus, it has a prospective application to water desalination and purification. This work opens a novel approach to the direct functionalization of graphene during the electro-exfoliation processes and to the subsequent assembly of the functionalized graphene.

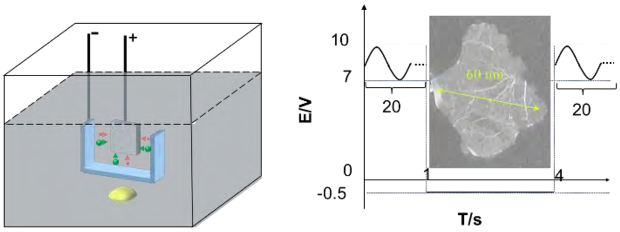

Fig. 1 the high-quality graphene produced by programmed potential modulations by balancing the ion intercalation/deintercalation, surface tailoring and bubbling dispersion processes in the electrochemical exfoliation of graphite.

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Bipolar electrochemistry for site-selective multifunctional modification of conducting objects

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Bipolar electrochemistry is a powerful technique for the asymmetric modification of conducting particles in the bulk. When placing a conducting object in an electric field produced by a pair of feeder electrodes, the potential distribution along the object polarizes it. If the potential difference between the extremities of the object is large enough, cathodic and anodic poles are created on which electrochemical reactions can occur and break the symmetry of the system. This "wireless" technique has been used for the bulk synthesis of Janus particles [1]. This method has also been used for the synthesis of ringed particles [2] and for the bifunctional modification of particles [3].

In this contribution, we present a method for the multifunctional modification of conducting particles using bipolar electrochemistry. Using AC potentials, it is possible to iteratively electrodeposit several metallic patches of different compositions on a conductive particle in a site-selective manner (Fig. 1). This method allows for the bulk synthesis of sophisticated asymmetric particles. The final objective of the work is the use of this symmetry-breaking concept to deposit four different patches in a tetrahedral geometry, which is impossible with any other deposition approach. This results in particles with a chiral character, analogous to an asymmetric carbon atom with four different substituents. Such objects could have numerous applications ranging from catalysis to chiroptics.

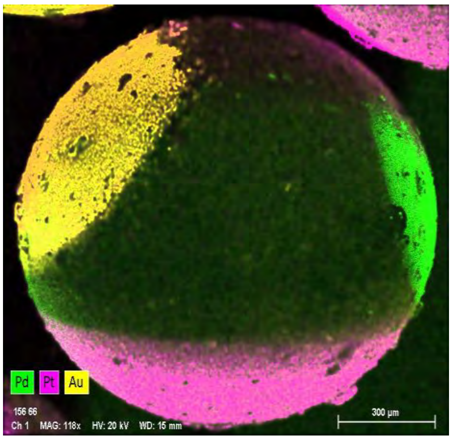

Figure 1 *EDX mapping of a glassy carbon particle functionalized with three different metallic patches: gold (yellow, left), platinum (pink, bottom) and palladium (green, right).*

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Porphyrin Trio-Pendant Fullerene Guest as an In Situ Universal Probe of High ECL Efficiency for Sensitive miRNA Detection

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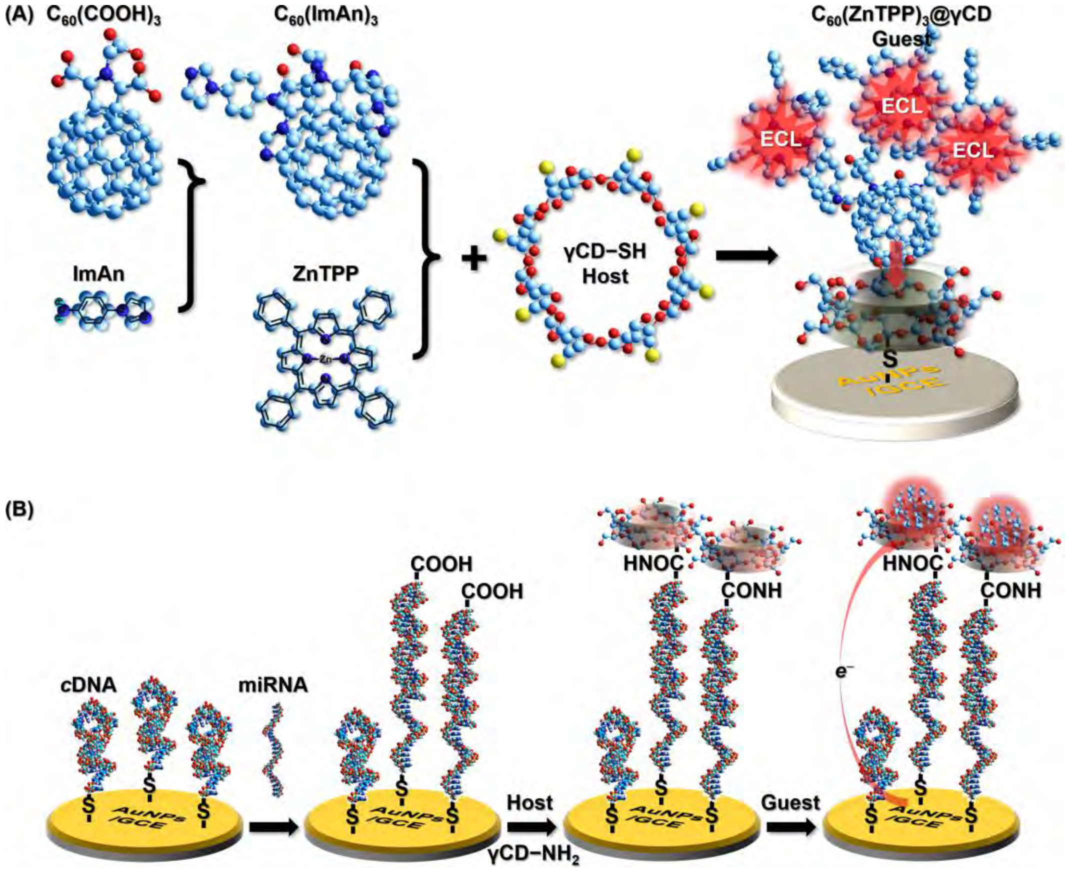
Herein, pyrrolidyl C_{60} derivative was recruited as an unadulterated and congruent nano-hub to converge three zinc porphyrins on its monopole. Such peculiar assembly was convinced via micro-imaging and spectrophotometry. Making the best of fullerenyl proficiency in catalytic singlet O_2 generation and excited-state preservation, a multiplied electrochemiluminescence (ECL) emission bursted out from the porphyrin trinity in a synergistic manner. Without any prebio-conjugation, this orderly ECL-active individual turned to anchor in the toroid of a peripherally modified gamma-cyclodextrin in a good shape match. From the facile direct mounting of the latter derives a universal bio-probing technique based upon such host-guest inclusion. Its binding pattern and the concomitant effects on interfacial properties were revealed by systematic process characterizations. Taking advantages of this uniform ensemble in both size and stoichiometry, an *in situ* terminal labelling strategy during the recognition-induced allosteric event came into being, which managed a neat signal enhancement for the detection of model miRNA marker. Even in real samples, the developed sensing approach could achieve high precision, comparable sensitivity and satisfactory selectivity. The adaptation of macrocyclic chemistry for refined biotransducers and efficient ECL amplifiers would offer a generic and potent alternative to the analyte-specified ECL indicator-receptor build in bioassays.



Scheme 1. (A) Synthetic route of $C_{60}(ZnTPP)_3$ the guest with precursor and intermediate models, and its inclusion in γCD−SH the host self-assembled on GCE/AuNPs. **(B)** Simplified miRNA assay workflow ended in *in situ* labelling with the signal indicator $C_{60}(ZnTPP)_3$@γCD.

Tracking CO_2 reduction products in real time

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Time-resolved characterization methods provide fundamental insights into electrode processes by capturing events that occur at short time scales. We recently developed the *electrochemical real-time mass spectrometry* (EC-RTMS) to determine gaseous and liquid products of electrochemical reactions shortly after their formation, with resolution in the order of few seconds [1]. After describing its basic components, I will present some representative examples of using EC-RTMS to monitor the products of CO_2 reduction under dynamic conditions, on various copper electrodes.

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Graphene supported metal phthalocyanine as an efficient noble metal free electrocatalyst for tetraelectronic oxygen reduction reaction

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Development of a noble metal free, efficient and durable electrocatalysts for oxygen reduction reaction (ORR) is a key requirement for a broader outreach of clean energy technologies like fuel cells, which also get utmost relevance in the present scenario of global warming. In this direction, nanocomposites of M-N-C molecular macrocycles and carbon nanomaterials has attracted tremendous attention because of simple and low cost synthesis methods and competitive ORR characteristics as compared to conventional platinum based catalysts [1]. In our ongoing studies, a nanocomposite based on cobalt phthalocyanine (CoPc) supported on reduced graphene oxide (rGO) has been synthesized by non-covalent functionalization followed by electrochemical reduction and its electrocatalytic properties towards ORR has been investigated. Through an extensive structural , topographic and morphological characterizations of the resultant CoPc/rGO composite, it was confirmed that electrochemical processing step was the key factor in synergically enhancing the ORR properties by simultaneously breaking the bigger aggregates of CoPc and reducing the oxygenated groups in GO, thereby improving the dispersion of CoPc nanoclusters on planar graphene support (Fig. 1a) [2]. Therefore, electrochemical reduction facilitates the improved exposure of ORR sites (metal center in CoPc), strengthens the π-π stacking in the composite and enhanced the conductivity of the catalytic materials. The ORR activity of the catalytic materials coated on a glassy carbon electrode were evaluated by voltammetric studies performed in a rotating ring disk electrode (RRDE) set up, which revealed a synergic ORR catalysis at the nanocomposite surface highlighted by larger current densities, 300 mV positive shift of the onset potential, and negligible generation of H_2O_2 as compared to CoPc and GO (Fig. 1b). Moreover, CoPc/rGO material has shown longer ORR catalytic lifetime than Pt based catalysts and resistance to methanol poisoning, making it an appropriate alternative of conventional ORR catalysts in methanol fuel cell.

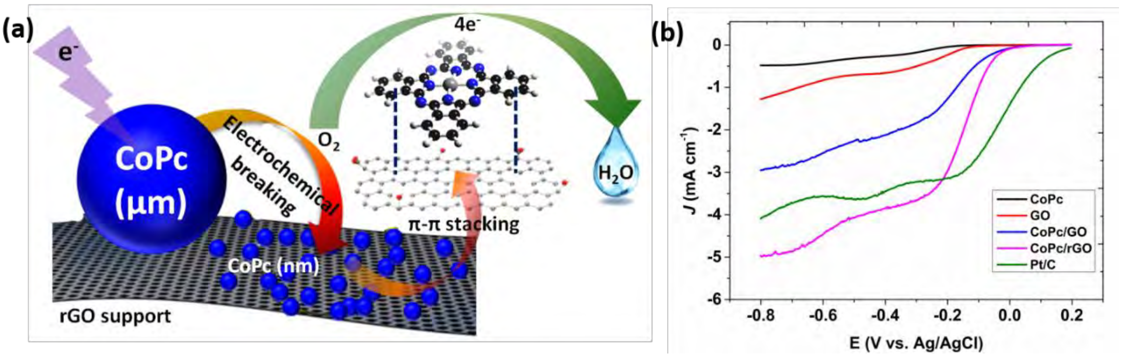

Fig. 1: *Schematic of electrochemically assisted dispersion of CoPc on graphene support and its ORR activity (a). Comparison of voltammograms of different catalytic materials in oxygen saturated 0.1 M KNO3 solution (b).*

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Surface functionalization by electrografting of aryls to tune the electrical characteristics of organic electronics devices

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Electrochemical grafting of aryl molecules on the electrode surfaces is a facile, well-controlled and extremely useful surface functionalization strategy to modulate the electrical characteristics of organic electronics devices. One of the preferred approach to realize such electrografting is via *in situ* diazonium formation from substituted aniline [1] to attach substituted benzenes on the conducting surfaces. Our endeavor in this direction is to functionalize Indium Tin Oxide (ITO) surfaces with benzene molecules bearing electron donating or accepting ligands to tune the electrical characteristics of the devices fabricated thereafter using such electrochemically processed ITO electrodes. Accordingly, Fig. 1 exhibits the cyclic voltammograms (CV) associated with electrografting of trifluoroethoxybenzene (TFEB) from the electroreduction of trifluoroethoxybenzenediazonium generated *in situ* from trifluoroethoxyaniline (TFEA) in an acidic medium. The progress of the electrodeposition is highlighted by the decrease in the reduction current with increasing CV cycles as a consequence of electrode conducting surface blockage by the relatively less conducting TFEB films. A simple schematic depicting grafting of TFEB molecules from TFEA precursor on the ITO surface during electrochemical processing has been shown in the inset of Fig. 1a. An optimization of this electrochemical step can result in the coating of a monolayer or a multilayer of such molecules on the electrode surface. The implications of such electrochemical grafting on the electrical properties of organic electronics devices like a Lutetium bis-phthalocyanine ($LuPc_2$) resistor can be profound. As a result of electrografting of TFEB film, the current-voltage (I-V) characteristics of the $LuPc_2$ resistor changed from an Ohmic to Schottky behavior (Fig. 1b), which can be attributed to the formation of an organic heterojunction interface because of electrografting [2]. Nature of these organic heterojunction interfaces and the built-in interfacial potential barrier so developed can be effectively tuned by the appropriate selection of substituents in the aryl molecules to be electrogrtaed at the electrode surface. Modulation of the interfacial potential barrier by electrografting in such organic heterojunction based devices and their applications in the development of conductometric gas sensors microsystem is the main scope of our ongoing work.

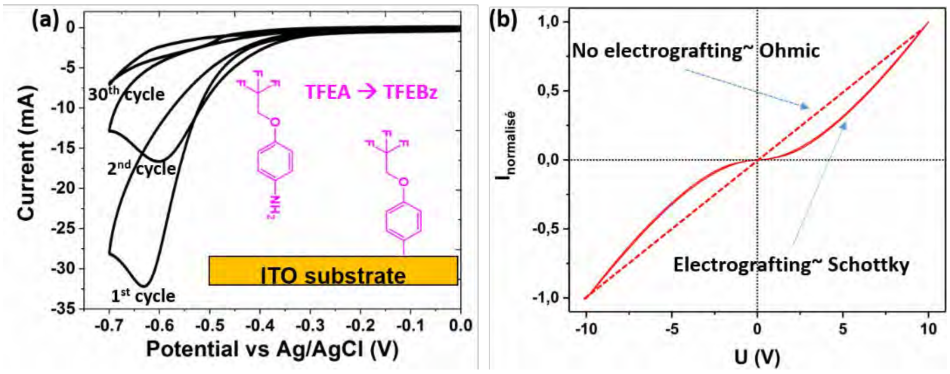

Fig. 1: *Cyclic voltammograms of ITO electrode in 2 mM* trifluoroethoxybenzenediazonium *in 1 M $HClO_4$ at a scan rate of 40 mVs-1 and schematic of electrografting of TFEB from TFEA on the ITO substrate in the inset (a). I-V characteristics of $LuPc_2$ resistor without and with electrografting of TFEB (c).*

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Tuning the Water Reduction Through Controlled Nanoconfinement Within an Organic Liquid Matrix

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The production of hydrogen through water splitting appears as an attractive way to face the intermittency of renewable energy power sources. In acidic media, the hydrogen evolution reaction exhibits very good kinetics on platinum electrocatalysts. However, in alkaline media, the HER exhibits relatively poor kinetics. After years of research efforts, a consensus has emerged at recognizing that the sole change in the energy of the surface intermediates cannot explain these different behaviors. Indeed, the structure of the interfacial water has been highlighted as a major parameter that controls the interfacial charge transfer, and thus the HER kinetics.[1-6]

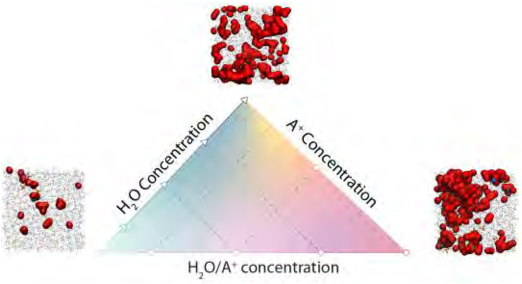

Figure 1. Snapshots of molecular dynamics simulations of water in acetonitrile for different water/salt ratios that illustrate the formation of *aqueous nanoreactors*.

To gain a deeper understanding on how these weak interactions affect the water reactivity, we have successfully explored a strategy consisting in confining water in an organic inert and liquid matrix (acetonitrile). Doing so, *aqueous nanoreactors* with controlled size and chemical compositions can be prepared. Hence, by playing on the water concentration, and/or on the supporting salt nature and/or concentration, the short and long-range environment of water molecules can be tuned, as we demonstrated by the combine use of classical molecular dynamics simulations, small-angle X-Ray scattering and NMR spectroscopy. Indeed, we show that water molecules can be isolated to independently study the influence of the water-cation interaction. Furthermore, by varying the size of the aqueous nanodomains, the amount of H-bonds formed between water molecules can be controlled, as illustrated in the **Figure 1**. Comparing this structural information with the measured activity for the water reduction on a platinum electrode, we can draw a picture of how the cation-water and water-water interactions compete, and how they govern the water reactivity at negatively charged electrodes. Overall, our results confirm the critical role of the transport of hydronium/hydroxides ions through the electrical double-layer on the water electrochemical reactivity. We believe that this simple chemical approach provides valuable information at the atomic level on the effect of water structure; these information were hardly attainable so far since it requires the use of complex experimental (temperature-jump, XAS, etc.) or computational techniques. Furthermore, developing such strategy to control the short- and long-range interactions in aqueous electrolytes will certainly prove very useful for studying other electrocatalytic reactions (OER, CO2RR, etc.).

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Synthetic Models of Hydrogenases as Electrocatalysts for Hydrogen Energy - from Molecules to Materials

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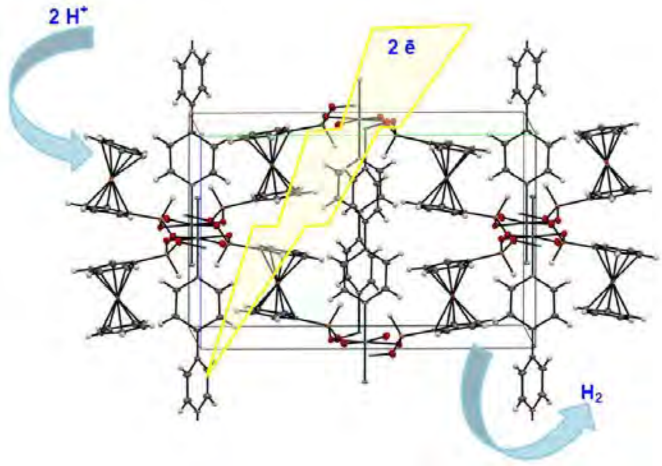
Replacing platinum in hydrogen fuel cells with earth abundant metals will be a crucial step toward the viable use of H_2 as a solar fuel. Understanding the factors that control the binding and heterolysis of H_2 to these metals can play a key role in improving H_2 activation/production. The [FeFe]- and [NiFe]-hydrogenases easily catalyze reversible interconversion between dihydrogen gas and protons and electrons at mild conditions. The structures of hydrogenase active sites have provided attractive targets for synthetic chemists to advance our understanding of the electronic structure and reactivity of these unique enzyme active sites. These efforts contribute to the synthesis of new Fe, Co and Ni catalysts for hydrogen oxidation or production that could have significant impacts on alternative and renewable energy solutions. In recent times, highly active widespread numerous electrocatalysts, both homogeneous or heterogeneous (immobilized on the electrode), such as transition metal complexes, heteroatom- or metal-doped nanocarbons, metal-organic frameworks, and other metal derivatives (calix[4]resorcinols, pectates, etc.), which are, to one extent or another, structural or functional analogs of hydrogenases, have been extensively studied as alternatives for Pt-based catalysts, demonstrating prospects for the development of a "hydrogen economy". The development of new biomimetic catalytic systems mimicking the action of metalloenzymes and biological nanoreactors is based on cage structures, which contain P, N and S donor atoms coordinated to metal atoms and form cavities composed of macrocycles. The maximum TOFs of hydrogen evolution from the best Ni catalysts reach 15200 s^{-1}, which exceeds the values for most synthetic electrocatalysts known in the literature and is comparable with the activity of natural hydrogenases. In recent years new materials have been created for fuel cells based on organometallic hydrogenase models, which have shown their effectiveness. So, the diaza-diphosphacyclooctane nickel(II) complex $[Ni(P^{Py}{}_2N^{p\text{-}Tol}{}_2)_2]^{2+}{}_2$ on Vulcan XC-72(C) functions as both the cathode and anode catalysts in polymer electrolyte membrane fuel cell with the cathode the power density of 14.66 $mWcm^{-2}$, which is the highest power density of the none-noble organometallic analogs. Membrane-electrode assemblies with a cathode catalyst made of a nickel sodium pectate complex PG-NaNi with maximum current density of 59 $mAcm^{-2}$ and power density of 5.9 $mWcm^{-2}$ have been successfully created. These results permit the development of environmentally friendly and stable catalysts for PEMFCs made of a available biological raw material. The main advances in the development of synthetic analogues of natural metal-containing hydrogenases and materials based on them are analyzed and summarized.



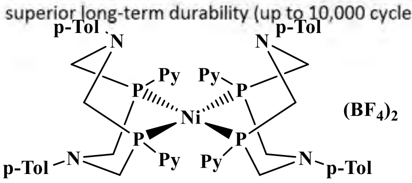
MbpyfcdHp (M=Ni, Co)

HER performances up to:

η 350 mV at the current density of 10 $mA \cdot cm^{-2}$;

TS of 60 $mV \cdot dec^{-1}$;

superior long-term durability (up to 10,000 cycles)



Acknowledgements
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Metalla-electrocatalyzed C−H Activation. Mechanistic Pathways Through Radical or High-valent Organometallic Intermediates

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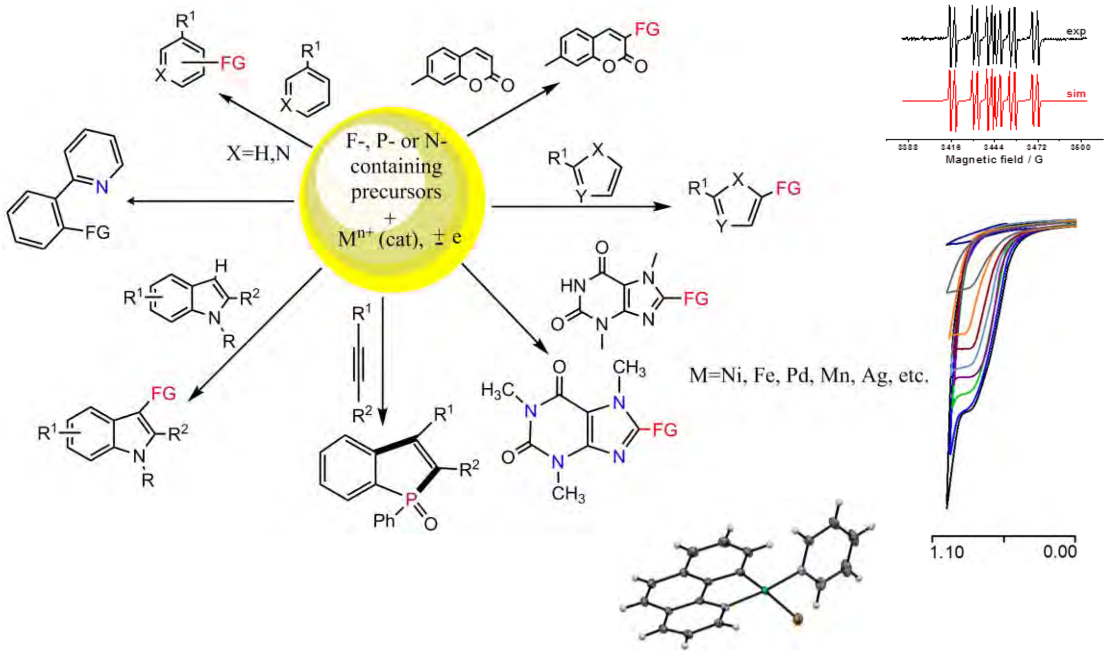
The transition-metal-catalyzed reactions are among the most valuable transformations in organic synthesis and are generally rests on catalytic cycle involving transition metal complexes at various oxidation states. In this context, electrochemistry provides advantageous methods both for synthetic purposes and for mechanistic investigation. Electrosynthesis is useful in transition metal catalysis to generate the active catalyst form without specially added reducing or oxidizing agents. Performed in mild conditions it offers more environmentally non-polluting alternatives to traditional organic synthesis. Electrochemical methods should be used in combination with spectroscopy techniques to provide detailed characterization of the intermediate species. The merger of metal catalysis and electrosynthesis, metalla-electrocatalysis, has been identified as a powerful strategy towards sustainable synthesis, which was substantiated by electrochemical metal-catalyzed C-H functionalizations in recent years. We propose a "green" one-step catalytic method for introduction of fluorine-, phosphorus- or nitrogen-containing functional groups to different compounds with C(sp^2)-H bonds assisted by electrochemical reduction or oxidation of metal complexes under mild conditions. The catalytically active form of metal complexes in high oxidation state (Ni^{III} or Pd^{III}, Fe^{II}, Ag^{I} etc.) is generated and regenerated on the electrode without specially added oxidants. Key organometallic intermediates are isolated and characterized. The patterns of these reactions have been established. High-valent cobalt^{IV}-bpy and other complexes stabilized in silica matrix were detected as catalytically active form and intermediate in cobalt-mediated oxidative C-H/NH cross-coupling reaction. Radical reaction pathways were found in some cases. Advantages of directed metal-induced aromatic C-H-fluoroalkylation, phosphorylation or amination are demonstrated.



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Oxygen Electrocatalysis by Transition Metal Spinel Oxides

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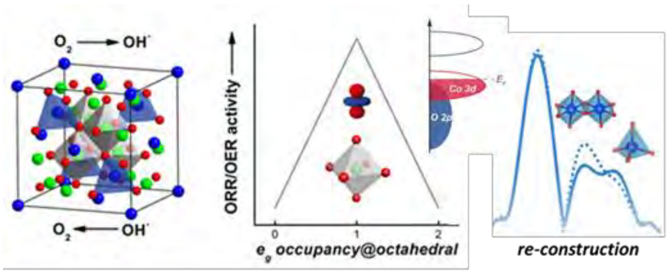
Exploring efficient and low-cost oxygen electrocatalysts for ORR and OER is critical for developing renewable energy technologies like fuel cells, metal-air batteries, and water electrolyzers. This presentation will present a systematic study on oxygen electrocatalysis (ORR and OER) of transition metal spinel oxides. Starting with a model system of Mn-Co spinel, the presentation will introduce the correlation of oxygen catalytic activities of these oxides and their intrinsic chemical properties. The catalytic activity was measured by rotating disk technique and the intrinsic chemical properties were probed by synchrotron X-ray absorption techniques. It was found that molecular orbital theory is able to well-explain their activities. The attention was further extended from cubic Mn-Co spinels to tetragonal Mn-Co spinels and it was found that the molecular theory is again dominant in determining the catalytic activities. This mechanistic principle is further applied to explain the ORR/OER activities of other spinels containing other transition metals (Fe, Ni, Zn, Li, etc.). The talk further gives insight on surface reconstruction on spinel oxides and how the bulk properties affect such reconstruction during OER. In addition, the talk will also discuss the possibility of the spin-selected charge transfer during oxygen electrocatalysis through transition metal oxides.



Dual-cathode Pulsed Current Electro-Fenton System: Enhancement for H_2O_2 Generation and Fe^{3+} Reduction

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Abstract: In conventional electro-Fenton (EF), high H_2O_2 generation and fast Fe^{3+} reduction rate are hard to simultaneously achieve on single cathode(**Liang et al., 2018**; **Deng et al., 2019**; **Xia et al., 2020**). Then a dual-cathode pulsed current EF is offered, where constant current imposes on gas diffusion cathode (GDE) and carbon felt alternately. In this system, GDE is mainly for H_2O_2 accumulation, while carbon felt is primarily for Fe^{3+} reduction. Optimal current density for H_2O_2 formation on GDE is 10 mA cm^{-2}, while it is 2.5 mA cm^{-2} for Fe^{3+} reduction on carbon felt. Switching time of 20 s is alternatively applied on each cathode (**Fig.1**). Under optimal conditions, H_2O_2 reaches 1400 μM, which is higher than the sum of H_2O_2 generation (1289.86 μM) on GDE and carbon felt in the conventional one. In addition, its energy consumption experiences the lowest level as 31.16 W h/mol H_2O_2. Moreover, a higher Fe^{3+} reduction rate (93.8%) is observed than the conventional single carbon felt system (71%). And total iron keeps stable since iron precipitation near-cathode vicinity is alleviated. A 98.5% sulfamerazine decay coupled with 85.6% mineralization confirms the superiority of the system, where a higher concentration •OH is detected compared to the conventional one. In conclusion, the proposed system coordinates H_2O_2 formation and Fe^{3+} reduction.

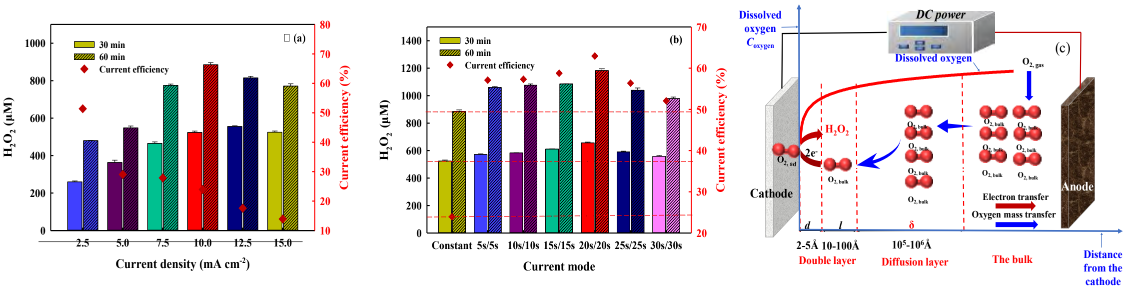

Fig. 1. (a) Effect of current density on H_2O_2 accumulation and related current efficiency (CE) at GED cathode, (b) influence of current mode on H_2O_2 accumulation and current efficiency (CE), (c) the whole process for two-electron ORR. Conditions: pH=3, $[Na_2SO_4]$ =50 mM, [oxygen flow rate] =300 mL min^{-1}, BDD sheet anode and GDE cathode (1 cm×2 cm).

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Flexible Sensors For Biomarker Determination In Sweat

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Biomarkers real time monitoring of biological fluids plays an important in preventive medicine [1]. Generally, bodily fluids serve as carriers for biologically active compounds and as medium in which biochemical reactions take place, therefore, a large range of information can be obtained by monitoring alterations to their composition in real time, or as response to external stimulus [2]. The most common example is the determination of glucose in blood. Particularly, sweat contains a large amount of small molecules and ions with biochemical interest, being an accessible biological fluid, continuous monitoring biomarker concentration in sweat represents an alternative to traditional methods avoiding discomfort to patients. To achieve this, wearable devices are designed for direct contact with the epidermis. The goal of of this work was to obtain flexible electrodes that allow direct contact with the skin by producing microscopic fibers of poly-methyl methacrylate (PMMA) by electrospinning [3]. Consequently, the microscopic fiber networks were metalized by thermal evaporation and magnetron sputtering with metals such as Au, Ag and Pd, [4], conductive and highly porous networks were obtained, which were then transferred onto polyethylene terephthalate flexible supports (PET).

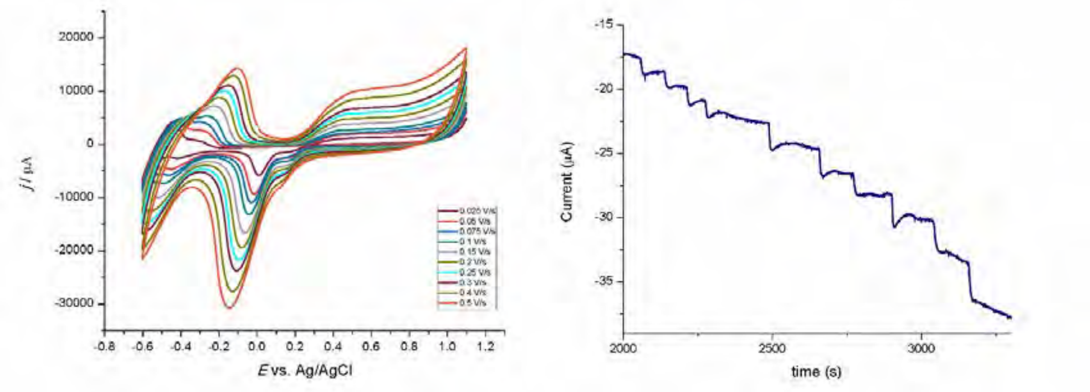

Fig. 1. A) Cyclic voltamograms of Pd/PMMA/PET electrode at different scan rates and **B)** amperometric response at -0.20 V after consecutive injections of 1 mM H_2O_2 in 0.1 M phosphate buffer pH 7.0, at Au/PMMA/PET electrode

Metalized flexible electrodes were applied for the detection of enzymatic products/coproducts like hydrogen peroxide by fixed potential amperometry. Optimum operational conditions were assed and analytical parameters were calculated for H_2O_2. PMMA metalized fibers were modified with different ionophores [5], in order to obtained sensors for target analytes such as Ca^{2+}, H^+, NH^{4+} and Cl^-. Ionophores immobilization procedure was optimized in order to improve sensitivity to analyte presence. The obtained interface was characterized by scanning electron microscopy with energy-dispersive X-ray spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy.

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The impact of nanowire geometry over the electric properties of ZnO nanowires based devices

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Fabrication of nanostructures with controlled morphology is extremely practical when it comes to applications like sensing devices. One of the most versatile nanostructures are semiconductor nanowires because they allow a control of key parameters such as chemical composition, diameter, length, dopping, electronic properties. Having been used in energy production, photocathalysis, light emitting devices, sensors or logic circuits, zinc oxide is one of the best candidates to build field effect transistors. This material is interesting due to its intrinsic physical properties, to its high occurrence/low cost and nontoxicity. [1, 2, 3, 4] Using a material which properties have been intensely studied makes it easier when one wants to observe the geometrical effect of ZnO nanowires over the electric response of a field effect transistor.

With the use of two types of polycarbonate membranes which have cylindrical pores (with the diameter of 200nm and 100nm), ZnO has been electrodeposited at two different deposition potentials. This resulted in four types of ZnO nanowires having different diameters (leading to a change of the surface/volume ratio) and having different concentration of Zn (leading to a change of the majority charge carriers).

Electron beam lithography (EBL) followed by sputtering techniques were employed in order to contact the nanowires to the electrodes. To understand how the size of the channels influences the properties of the final device, for each of the four types of nanowires used, two different channel lengths were made using EBL.

Scanning electron microscopy, energy-dispersive X-ray spectroscopy, reflection and X-ray diffraction were used to characterize the nanowires and the field effect transistors obtained. Thus we were able to analyze the morphology, the composition, the structure and the value of the bang gap in order to have a better understanding over the electrical measurements that have been made at different temperatures. The goal of this study is to functionalize the field effect transistor with electrodeposited ZnO nanowire channel in order to obtain a device which is sensitive to organic compounds such as biotin.

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Influence of superimposed magnetic field on Co-Fe alloy 1D nanocone array electrodeposited in AAO template.

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One-dimensional (1D) nanostructures such as nanotubes, nanopores, nanodots and nanocones are fabricated using porous anodic alumina oxide (AAO) template produced in two-step anodization. Due to their large active surface area and small geometrical size these materials are characterised by better catalytic properties than bulk material [1]. Alternating cycles of the anodization in oxalic acid and pore widening process in phosphoric acid led to obtain conical nanopores templates. To obtain free standing nanocones the Al_2O_3 template has to be chemically etched.

Co-Fe alloy nanocones were electrodeposited in AAO templates. The magnetic field with different intensity has been superimposed during electrodeposition. The hydrodynamic conditions during electrochemical process are changed by the magnetic field. This cause the modification of composition and morphology of Co-Fe nanocones. The active surface area of samples were calculated from SEM photos. The electrocatalytic properties of fabricated nanostructures were measured in 1M NaOH and compared with bulk materials.

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Acknowledgement

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Determination of bisphenol S, simultaneously to bisphenol A in different water matrices or solely in electrolyzed solutions, using a cathodically pretreated boron-doped diamond electrode

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As the hazardous effects of bisphenol A (BPA) are being revealed, alternative "BPA-free" products are coming out. Bisphenol S (BPS) is one of the most widely used substitutes for BPA. However, it has been shown by recent studies that BPS could be unsafe similarly to its analog BPA[1]. The widespread use of BPS and BPA and their persistence in the environment make them arise as worrisome pollutants. In this context, analytical methods capable of simultaneously determining BPS and BPA in different environments liable to contamination, like waterbodies, are required. In this work, a simple, accurate and environmentally friendly method for the simultaneous determination of BPS and BPA was developed and validated. The determination was performed by square-wave voltammetry (SWV) using a cathodically pretreated boron-doped diamond (BDD) as the working electrode, with 0.1 mol L^{-1} H_2SO_4 as the supporting electrolyte. Under optimized conditions, a wide linear working range ($R^2 = 0.999$) from 0.20 to 80.0 mg L^{-1} (8.0×10^{-7} to 3.20×10^{-4} mol L^{-1}) with a limit of detection ($S/N = 3$) of 0.060 mg L^{-1} (2.4×10^{-7} mol L^{-1}) was attained for BPS. For BPA, a linear correlation ($R^2 = 0.992$) from 0.10 to 50.0 mg L^{-1} (4.4×10^{-7} to 2.19×10^{-4} mol L^{-1}) was attained, with a limit of detection of 0.030 mg L^{-1} (1.3×10^{-7} mol L^{-1}). Figure 1 presents the baseline-corrected square-wave voltammograms for both concentrations being varied simultaneously (Fig. 1A), and the I_p vs. [BPS] or [BPA] plots (Fig. 1B) for the lower concentrations of the linear working ranges.

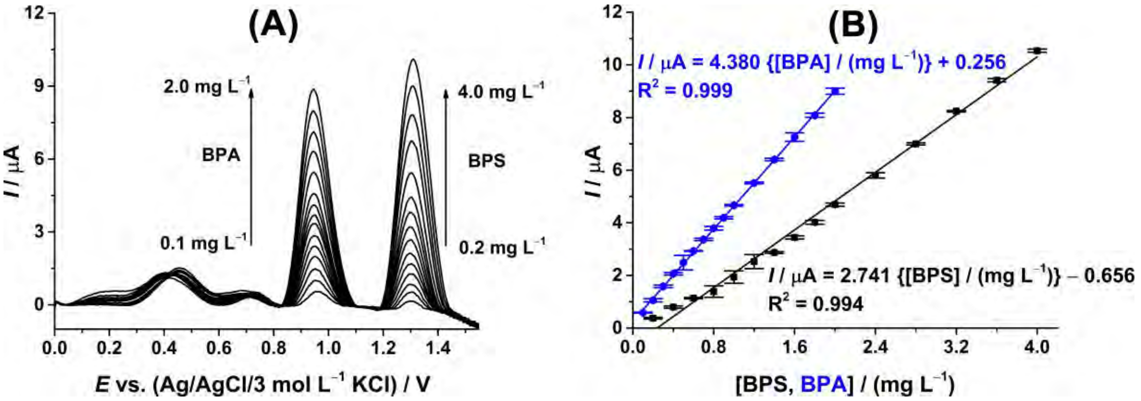

Fig. 1. (A) Baseline-corrected square-wave voltammograms at the cathodically pretreated boron-doped diamond electrode for the simultaneous addition of increasing concentrations of BPS and BPA in 0.1 mol L^{-1} H_2SO_4. **(B)** Respective calibration curves for BPS (black) and BPA (blue) obtained from the simultaneous addition data. SWV parameters: amplitude: 50 mV, frequency: 60 Hz, step potential: 6 mV

As can be seen in Figure 1, independent increases of the oxidation current peaks were observed with a linear behavior ($R^2 \geq 0.994$). Thus, it can be concluded that the simultaneous determination of BPS and BPA is feasible in the given conditions. The method was applied to the simultaneous determination of BPS and BPA in real water samples, with minimum sample preparation processes (only dilution and acidification). Excellent recovery values were achieved, ranging from 94.9 to 98.8%. Additionally, the method was applied to the monitoring of the electrochemical degradation (anodic oxidation) of BPS using a recirculating flow system fitted with a BDD anode. The decay of [BPS] with time was also checked by an HPLC method, with results statistically similar to those obtained by the proposed electroanalytical method. Hence, the proposed method is a reliable, greener and low-cost alternative to monitor simultaneously BPS and BPA in aquatic matrices or only BPS in wastewater treatment processes.

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Hydrogen Oxidation Reaction on Ni-based materials: influence of the surface state of Ni *vs* electronic effect of a second metal

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Recent years have witnessed significant increase in the interest towards H_2-O_2 (air) anion exchange membrane fuel cells (AEMFCs), largely stimulated by the development of AEMs and platinum group metal (PGM) free catalysts for the hydrogen oxidation reaction (HOR) [1-7]. The latter are typically based on nickel, benefiting from its low cost and high corrosion stability in alkaline media. Since pure metallic Ni demonstrates rather poor performance in the HOR, various means have been suggested for its ‘activation’. Alloying of Ni with a second metal is one of the most popular approaches [1-3]. The activity enhancement is usually attributed to an electronic effect of the second metal, while the exact physical origin of this ‘electronic’ effect has not been fully understood yet. Meanwhile, such an understanding is of paramount importance for the development of efficient anode catalysts for AEMFCs.

In this work, we prepare a series of monometallic Ni/C and bimetallic NiMo/C and NiCu/C catalysts using an incipient wetness impregnation. Their HOR activities are compatible with the best reported PGM-free catalysts [3-6]. By complementing electrochemical studies with a thorough physicochemical analysis (HR-(S)TEM, EDS, XRD, XPS) of the prepared catalysts before and after their reductive treatment, by performing Monte Carlo simulations of bimetallic nanoparticles we demonstrate several important findings. First, we show that the surface state of monometallic Ni/C catalysts is a determinant factor for their specific activity in the HOR independent of the synthetic procedure (electrodeposition or chemical deposition). Second, more importantly, by comparing HOR activity of mono- and bimetallic (NiMo/C and NiCu/C) catalysts either taken from air or subjected to thermal reduction by H_2 right before the electrocatalytic measurements we discover that the state of the Ni surface (metallic *vs* partially oxidized) has stronger influence on the HOR than the presence of the second component (Fig. 1). At the same time, the second metal might help to maintain (up to some extent) the desired state of Ni surface in the resulting catalyst thus affecting its stability in the HOR.

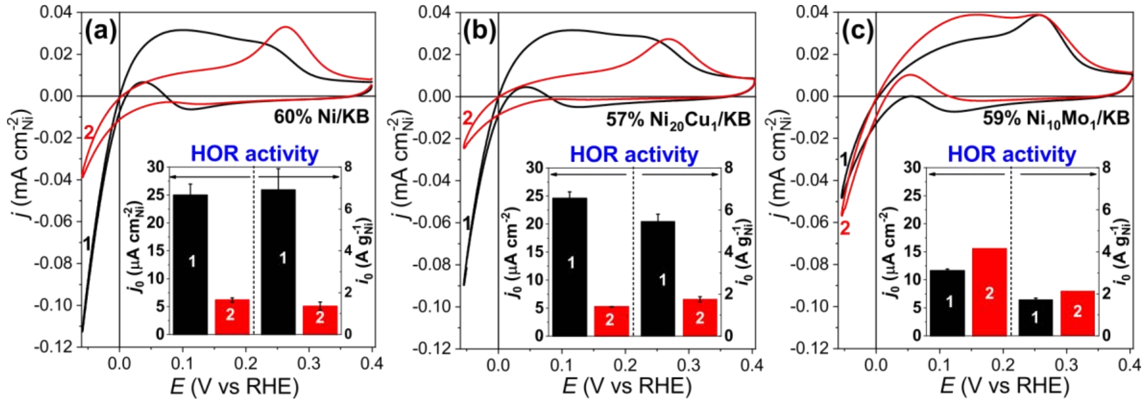

Figure 1. HOR polarization curves (0.1 M NaOH, 25 °C, 5 mV/s, 1600 rpm) and the corresponding surface- and mass-normalized HOR exchange current densities (insets) for Ni/KB (a), $Ni_{20}Cu_1$/KB (b), $Ni_{10}Mo_1$/KB (c) catalysts either taken from air (1) or subjected to thermal reduction by H_2 (2).

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Formation and Reactivity of Phosphorous Acid on Platinum at Conditions Relevant to HT PEM Fuel Cell

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Proton-conductive membranes, based on doping of polymers with H_3PO_4, are often utilised in fuel cells operating above the temperature of 120 °C. The main advantage of operating at elevated temperatures is feasible heat recuperation and absence of demanding water regime. Particularly, high temperature fuel cell with proton-conductive membrane (HT PEM FC), operating in temperature range of 120 to 180 °C, is one of promising types. It utilizes Pt nanoparticles as a catalyst on both electrodes, hydrogen as a fuel and oxygen as an oxidant. In membrane, H_3PO_4 is used as a dopant with high proton-conductivity and, supposedly, high stability. However, the stability has been questioned in recent years, as electrochemical reduction of H_3PO_4 on a Pt surface can lead to formation of H_3PO_3 and other phosphorus compounds like Pt-P.

One of the profound problems related to HT PEM FC is degradation of Pt catalyst on the cathode and, consequently, diminishing of Pt surface area during the operation. The degradation of Pt nanoparticles proceeds via Ostwald ripening mechanism, with Pt dissolution as rate-determining step [1]. To avoid deterioration of cathodic Pt surface area, general recommendation is to avoid voltage cycling [2], induced by the start-up and shut-down procedure. At this point, it is important to stress that at such conditions, reduction of H_3PO_4 following by the oxidation of reduction products, takes place on the cathode [3]. The effect of this process on the catalyst is still undescribed, also due to lack of data on electrochemical behaviour of H_3PO_3 and Pt-P on a Pt surface. What is confirmed, however, is chemical behaviour of H_3PO_3 in terms of its reducing and adsorbing properties [4]. Therefore, the impact of H_3PO_3 on a degradation of Pt nanoparticle catalyst is potentially significant.

The goal of this study was the description of H_3PO_3 formation and electrochemical behaviour on bulk Pt electrode in concentrated H_3PO_4 electrolyte at temperatures above 120 °C. Experiments were performed in three-electrode arrangement, using voltammetric methods. Important features of H_3PO_3 behaviour were evaluated, including its oxidation kinetics and adsorption isotherms on a Pt electrode surface and interaction with oxidised Pt surface. Results proved that H_3PO_3 presence in Pt/H_3PO_4 system at elevated temperatures has, indeed, high impact on Pt surface reactions dynamics. In the next step, experimental data will be verified using gas-diffusion electrode in half-cell arrangement.

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Adsorption of Guanine on Au(111) Electrodes Studied by in situ Surface-Enhanced Infrared Spectroscopy

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DNA-based biosensors attract an enormous interest due to their potential applications, such as detection of DNA base damage in clinical diagnosis or evaluation of DNA-drug interaction mechanisms.[1] Understanding the adsorption of individual DNA bases on solid substrates is of fundamental interest since different structural conformations adopted by DNA can lead to different interactions, changes the accessibility of drugs to the DNA grooves, or promote different rates of hybridization.[1] These conformational changes in DNA can be induced by changes in the acid-base or tautomeric equilibria of the bases, originated either by the interaction with the substrate or by the application of an external electric field. Guanine is one of the DNA bases that undergoes two acid/base equilibria, pKa values 4.2 and 9.5, (Figure 1) and may present several tautomeric forms in aqueous solutions.[2]

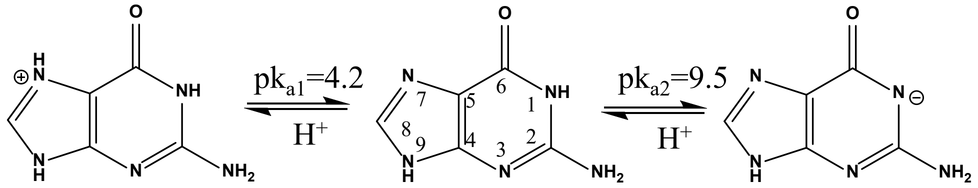

Figure 1. Acid-base equilibria of guanine

In the present work, we report a spectroelectrochemical study by in situ Surface-Enhanced Infrared Absorption Spectroscopy in the Attenuated Total Reflection mode (ATR-SEIRAS) to understand and characterize the guanine adsorption on gold thin-film electrodes from solutions at two pH values under the first pK_a using H_2O and D_2O as solvents. The spectra are interpreted on the basis of DFT calculations over different acid-base and tautomeric forms of the molecule.

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Electrode Processes in Lithium-Mediated Electrochemical Nitrogen Reduction

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Ammonia is one of the most important industrial chemicals, with *ca* 1 % of the world's energy being used for its production. It is mainly used to produce artificial fertilisers, which are essential for the sustenance of the growing global population. Even though molecular nitrogen is readily available, the N_2 molecule is notoriously inert and its reduction to NH_3 is challenging. NH_3 is currently produced in the energy intensive Haber-Bosch process, which requires high temperature and pressure in order to activate N_2. This necessitates production in large, centralised plants. Considering this, there is a certain interest in the development of alternatives which could be implemented in a more decentralised manner. The electrochemical reduction of ammonia would be an attractive option, as electrochemical potential could be used to drive the reaction, enabling on-site production using electricity from renewable energy sources. This prompted widespread scientific interest for the investigation of this reaction. The field of electrochemical nitrogen reduction (N_2RR) was, and to a large degree still is, struggling with numerous issues regarding reliable NH_3 detection, signal-to-noise ratio, contamination and reproducibility. Nonetheless, Li-mediated N_2RR in non-aqueous electrolytes has been shown to be a viable method to reduce molecular nitrogen to ammonia[1], at least on the laboratory scale. It is generally assumed that in the process the electrodeposited Li reacts with dissolved nitrogen forming Li_3N, which subsequently receives protons from a proton carrier, such as an alcohol, forming NH_3 and an alkoxide, Figure 1A. The implementation of an electrochemical quartz crystal microbalance (EQCM) allows the direct measurement of the deposition on the electrode, which coupled with isotope labelling experiments, can shed light on these processes. The monitoring of mass deposition on the electrode surface during the potential scan using an EQCM, Figure 1B, can give indications about the SEI formation, possible side reactions, and information about the Li deposition process and subsequent reactions[2]. While nitrogen reduction in ambient conditions is an interesting prospect, this electrochemical system does have certain limitations: only modest Faradaic efficiencies were achieved, it requires oxygen- and water-free conditions, non-green solvents are usually used, and the proton carriers are irreversibly lost in the reaction. The prospects of overcoming these and other issues will be discussed, and possible directions for future research will be laid out.

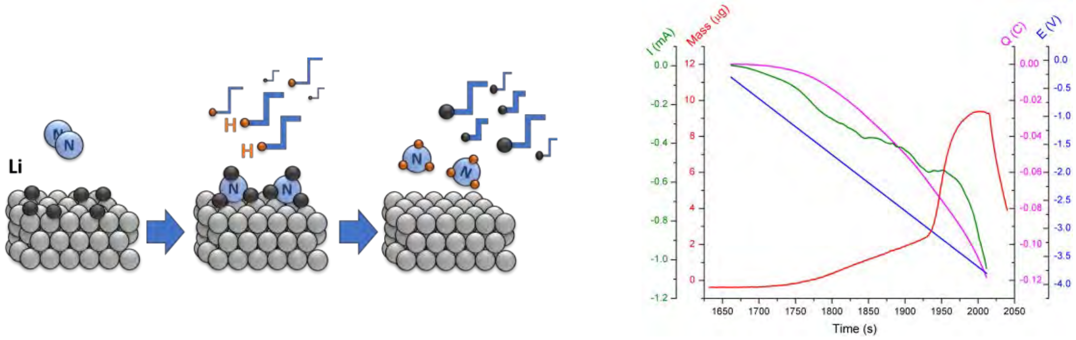

Figure 1: (A) The proposed reaction scheme (B) Mass deposition, current and charge passed during potential scan as detected by EQCM

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*these authors contributed equally

[2] To be determined. In preparation.

CO_2 Reduction Reaction on Cu_2O Electrodes: High Alcohol Selectivity at Low Overpotential Accompanied by Current Oscillations

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The electrochemical reduction of CO_2 (CO2RR) provides an attractive means to synthesize fuels and feedstock chemicals in a sustainable way. However, a large-scale utilization is still hampered by the low selectivity of most catalysts for many of the potential products as well as high overpotentials. So-called Cu oxide-derived Cu (Cu-OD) has been identified as promising electrode material, overcoming in part these limitations. The catalytically active Cu-OD electrode is obtained operando from Cu_2O primary material at CO2RR electrode potentials and exhibits a high selectivity for C_2 products, in particular for ethylene. On the other side, it has been believed to be inactive towards alcohol formation [1]. In this paper we present a modified protocol for the generation of Cu-OD electrodes that is highly selective for alcohol formation and yields current densities as high as 300 mA/cm^2 geometrical area at overpotentials as low as -0.7 V_{RHE}.

The Cu-OD catalyst was electrochemically synthesized by sequential depositions, leading to a high surface area Cu_2O (with a roughness factor r = 35.2 for the electrochemical surface area). Characterization of the material and the Cu-OD surface by XPS, showed that the catalytically active surface has an unusual large number of oxygen vacancies.

The CO_2RR was measured in a CO_2-saturated, 0.5 M K_2CO_3 electrolyte. CO_2RR current densities obtained were in the order of 10 mA cm^{-2}_{ECSA}, i.e. 350 mA $cm^{-2}_{geometrical}$, at -0.70 V_{RHE}, one of the highest activities ever reported at this overpotential [1,2]. This high current value is observed together with another feature, so far not observed during CO_2RR, namely current oscillations , manifesting that for this set of conditions CO_2RR presents non-linear behavior. Liquid products analysis was performed by nuclear magnetic resonance (NMR) after keeping the electrode for 1h under oscillatory conditions. Ethanol (EtOH) and methanol (MeOH) were the main products, with faradaic efficiencies of 33.1 (EtOH) and 31.7 (MeOH) %. This amounts to activities of -3.35 (EtOH) and -3.20 (MeOH) mA cm^{-2}_{ECSA} or -119.26 (EtOH) and -114.18 (MeOH) mA cm^{-2}_{geom} (see table I). Only when the reaction rate exhibited oscillations were these high activities observed. XPS data suggested that under these highly active and oscillatory conditions the density of oxygen vacancies had increased compared to less negative potentials, pointing to a close relation between oscillatory conditions, alcohol selectivity and degree of oxygen evacuation.

Table 1. Faradic efficiencies (FE) and activities (as function of geometrical area and ECSA) for alcohols obtained during CO_2RR at 0.70 V_{RHE}.

Product	FE / %	Activity / mA cm^{-2} $_{geom}$	Activity / mA cm^{-2} $_{ECSA}$
MeOH	31.7	-114.18	-3.20
EtOH	33.1	-119.26	-3.35

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Pore Network Modelling of Invasion Processes in Electrochemistry

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Flow in porous media has widespread importance in various fields of science. For the understanding of transport phenomena within a porous medium, at a meso- or microscale, Pore Network Modelling (PNM) has been of great use. PNM has been prevalent in geo-material and drying applications for a long time. In the recent time, PNM has found its way into electrochemistry; precisely in analyzing the two-phase transport within the porous components of fuel cells, electrolyzers or batteries. The efficiency of these systems depends significantly on the transport kinetics and the evolving dynamic distributions of gas and liquid e.g. inside the catalyst layer, where the electrochemical reactions occur. For example, in the case of electrolysers, the oxygen gas produced at the anode must be removed so that the water supply adequately persists. The oxygen coverage of the catalyst layer obstructs the water supply towards the reaction zone[1]. This can lead to a decrease in the rate of reaction. On the contrary, in fuel cells, water produced as the result of the electrochemical reaction must be removed efficiently[2]. For these systems, to be more marketable and serve as a viable option for future energy problems, they must be optimized in terms of performance. The mass transfer through these diffusion and transport layers thus becomes an important issue to be investigated for a better understanding of the transport limitations, as they play a major role in defining the performance of these systems. This requires a deep understanding of the pore scale distribution of gas and liquid phase at different operating conditions.

PNMs conceptually represent the porous media. Micro computed tomography is used to extract the required information about e.g. pore size distribution, pore connectivity, pore shape etc. The model uses this information to generate an interconnected network of pores. This network of pores portrays the voids of the porous medium through which the phase transport occurs. Relevant two-phase flow physics are used to study the transport limitations at microscale. Compared to existing macroscopic models; PNM is suitable for low capillary numbers, takes wetting characteristics into account and resolves the invasion process on the pore scale. It can be shown by PNM that the tortuosity of the gas/liquid paths and permeabilities essentially depend on the pore structure, local temperature and wettability of the porous medium as well as local pressure differences. Use of PNM for imbibition and drainage phenomena allows the study of the correlation between material properties and operation conditions and the relevant effective transport parameters, and it can also be used to parameterize the macroscopic continuum models. Thus, PNM can also facilitate optimization of the structural parameters of these materials that are required for an efficient operation.

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Nanoporous gold-palladium: A binary alloy with high catalytic activity for the electro-oxidation of ethanol

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Nanoporous gold (NP-Au) is a promising versatile material that can be used in many fields, a result of its high conductivity, large surface area, and excellent stability. NP-Au is commonly functionalized in combination with other materials; however, difficult syntheses are obstacles to catalyst development. In this presentation, a simple method for the fabrication of binary nanoporous gold-palladium (NP-AuPd) with a tunable Au/Pd ratio is developed [1]. Ternary alloy films of Au-Pd-Mg are prepared by sputter deposition and Mg is dissolved from the alloy to make nanoporous structures. The Au and Pd in NP-AuPd are evenly distributed over the entire structure. The electro-catalytic activity of the developed NP-AuPd is evaluated by oxidizing ethanol in alkaline media. The optimized NP-AuPd shows remarkable electro-catalytic activity and excellent stability. The nanoporous structure not only increases the number of reaction sites and mass transfer, but it also enhances the durability of the catalyst. The developed method can be extended to the preparation of binary nanoporous thin films with controlled compositions and desired catalytic activities.

[1] K.-U. Lee, J. Y. Byun, H.-J Shin, S. H. Kim (submitted)

Metal Air Battery using Expanded Natural Graphite Sheet as Cathode at the emergency

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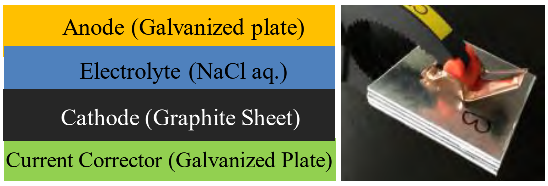
Metal air battery is superior to lithium secondary ion battery because of none danger of ignition and possibility of keeping for a long time. We think that it has many problems for development of secondary battery. However, we reported that metal air battery using expanded natural graphite sheet as cathode and galvanized plate as anode is promising device for primary battery for backup power supply and emergency one [1]. Discharge capacity of this battery is 2.1mAh/cm^2 which value is about three times than that of Bincho charcoal metal air battery which have been used science teaching material. We hope that this battery can be used a lot of applications, such as a light-emitting and smart phone charging and so on at the emergency, because DC 12 V output can be obtained in 15 cells connected in series.

Maine parts of this battery are expanded natural graphite sheet for cathode, galvanized plate for anode and electrolyte. Expanded natural graphite sheets have been using for gasket and heat radiation materials because of high thermal conductivity, high electric conductivity, physical and chemical stability, workability and so on. We can easily and cheaply get the large size with the wide of 1.3m and long of more than 100m. Galvanized plate is very cheap and physical and chemical stability, too. These materials can be kept for a long time without particular environment. We only need to prepare the electrolyte due to fabricate this battery at the emergency.

In this paper, characteristics of metal air batteries using expanded natural graphite sheet as cathode and galvanized plate as anode with various electrolyte has been investigated for a power units at the emergency. The standard electrolyte was used 10 % sodium chloride water solution absorbed to the filter paper with thickness of 0.7 mm as a separator. We attempt to use various liquid, which we can easily get at the emergency, as an electrolyte, such as normal water, sports drink, and so on. The separators, such as glass wool and various paper, were selected with the same thinking for electrolyte. The cell size was square of 25cm^2. The standard properties of the primary battery, such as discharge capacity, voltage and internal resistance, were measured.

Figure 1 shows the standard single cell structure and its apparatus. The oxygen gas as the activation material for the cathode can be get from side edge of expanded natural graphite sheet. Figure 2 shows the discharge properties of metal air batteries using electrolytes of 10 % sodium chloride water solution, tap water, sports drink, and so on, with separators of filter papers. When sports drink are used for electrolytes, discharge capacities are larger than that of using 10 % sodium chloride water solution that is standard electrolyte. Furthermore, it was found that metal air battery using electrolyte of the other solution could be working for LED light emitting.

We hope that this battery can be used at the emergency, because DC 12 V output can be obtained in 15 cells connected in series and we can easily get all battery parts at the emergency.



Structure

Apparatus

Fig.1 Standard single cell of metal air battery.

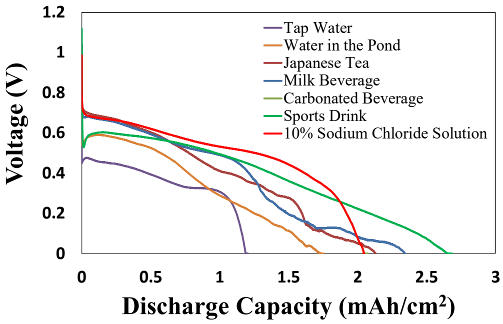


Fig.2 Discharge capacity of metal air battery using various electrolyte.

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Defective Graphene Overlayers on Pt(111) Enhance Hydrogen Evolution Reaction (HER) in Aqueous H_2SO_4

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The production of hydrogen through water electrolysis using renewable electricity is a promising carbon-neutral technology. We present insights into the hydrogen evolution reaction (HER) in aqueous H_2SO_4 (0.005 to 0.5 M) on Pt(111) on Graphene/Pt(111) under ambient temperatures and pressures. Graphene was grown on Pt(111) using chemical vapor deposition (CVD) of hydrocarbons and characterized using scanning electron microscopy (SEM) and Raman spectroscopy [1].

Cyclic voltammograms (CV) and HER currents of Pt(111) in H_2SO_4 were quantitatively benchmarked to literature to ensure reproducibility and comparability of kinetic measurements [1-3]. CV sweeps (0.005 to 0.5 M, 23°C, 0.1 to 0.8 V_{RHE}) indicate that graphene overlayers are selectively permeable to H^+ ions in the electrolyte, allowing H^+ ions into the confined layer between Pt(111) and graphene while excluding SO_4^{2-} and other anions [2]. The extent of defects in graphene was quantified by integrating the anion adsorption region from CVs. The anion adsorption coverage on electrochemically pre-treated Graphene/Pt(111) (250 cycles between 0.1 to 1.2 V_{RHE} in 0.005 M H_2SO_4) increases with HER reaction time at a rate of ~$3*10^{-6}$ $mol_{anion}\ mol_{Pt}^{-1}\ s^{-1}$ while untreated Graphene/Pt(111) exhibits a slower increase of ~$5*10^{-7}$ $mol_{anion}\ mol_{Pt}^{-1}\ s^{-1}$. Though the defect generation rate is slower on untreated Graphene/Pt(111), a sudden order-of-magnitude increase in anion coverage is observed between 9 to 12 hours of HER. In contrast, no sudden increase in the anion capacity is observed on electrochemically pre-treated Graphene/Pt(111) for up to 15 hours of HER.

Initial HER currents on both pre-treated and un-treated Graphene/Pt(111) are slower than Pt(111) by 1 to 2 orders of magnitude (0.005 to 0.5 M, 23°C, -0.08 V_{RHE}). HER currents on both pre-treated and un-treated Graphene/Pt(111) increase with HER reaction time to values equal to or higher than that of Pt(111), concurrent with increasing graphene defects as probed using CV and SEM. Unchanged HER Tafel slopes and $[H^+]$ reaction orders suggest the same HER mechanism between Pt(111) and Graphene/Pt(111). We postulate that untreated graphene is mass transfer limited and HER currents transition from mass transfer limited to kinetics limited with increasing graphene defects. Li et al. computes that a graphene overlayer would weaken the hydrogen binding energy to Pt(111), shift the reaction closer to the peak of the HER volcano plot, and thus increase HER currents [6,7]. Though our results agree with prediction, we cannot negate other possible explanations for the observed increase in HER rate. These results demonstrate the promise of overlayer and confinement modifications in designing catalysts with properties closer to achieving optimum currents.

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Electrochemical characterization of fiberglass membranes modified with polyelectrolytes used as the support for the electrified liquid-liquid interface.

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The interface between two immiscible electrolyte solutions (ITIES) is a system which allows the control of a potential difference between two adjacent liquid phases. It can be used to explain the charge transfer reactions happening at this soft junction. The example of ITIES, also used in this work, could be an interface formed between the aqueous solution of sodium chloride (water phase) and a solution of highly hydrophobic salt (bis-(triphenylphosphoranylidene)-ammonium tetrakis-(4-chlorophenyl)-borate) dissolved in 1,2-dichloroethane (organic phase). Systems based on ITIES found a very few applications in e.g. sensing [1], redox catalysis [2], fundamental studies [3] among many other [4].

In our work, we have used three polyelectrolytes: polyethyleneimine (PEI), poly(styrene sulfonate) (PSS) and polyhexamethylene guanidine (PHMG) to create the thin polymer multilayer on a surface of fiberglass membranes. In first, the interfacial behavior of polyelectrolytes alone was studied at the unmodified liquid – liquid interface. Next, the fiberglass membrane was activated in 1M NaOH in order to assure the negative charge at its surface. Following that, the first polyelectrolyte layer – branched PEI – was deposited by simply immersing the membrane into PEI solution. The negatively charged PSS and the positively charged PHMG were then alternatively added using layer-by-layer (LBL) technique. When such membrane was used as a support for the ITIES, interesting current patterns – typical for miniaturized junctions – were recorded. AFM and SEM revealed the membrane surface morphology. Finally, the membrane sieving properties were examined. In this respect we have used a series of model quaternary ammonium cations (tetramethylammonium, tetraethylammonium, tetrapropylammonium, tetrabutylammonium). In future, our platform can find applications in liquid – liquid interface miniaturization, molecular separation and sensing.

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Novel Iridium Based Catalysts on Ti$_2$AlC Support as Cost Effective Solution for Green Energy Production by Water Electrolysis

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Ultra-thin iridium layers were deposited on Ti$_2$AlC substrate from the solution containing K_3IrCl_6 and Na_2SO_4 (pH 6.2) at 70°C by using cyclic voltammetry. These novel materials were tested as the catalysts for hydrogen production – well known as an environmental friendly, green energy fuel. Namely, the hydrogen evolution reaction (HER) was investigated both in acid and alkaline electrolytes - 0.5 mol dm^{-3} H_2SO_4 and 1 mol dm^{-3} KOH. A variety of different thickness samples were characterized by physical-chemical characterization, as well as by electrochemical techniques.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) confirmed that the nucleation of Ir was not fast, indicating practically epitaxial growth of the deposit on Ti$_2$AlC substrate. The presence of cracks was detected in the thickest Ir layer (~ 260 nm) probably caused by increase of tensile strength. Metallic iridium was detected by X-ray photoelectron spectroscopy (XPS) at the surface of all samples, indicating complete reduction of iridium ions to zero valence state.

The HER was investigated by polarization and electrochemical impedance spectroscopy (EIS) measurements. Polarization curves were characterized with the low Tafel slopes of (between -10 and -20 mV dec^{-1}) up to about -0.1 A cm^{-2}, while at higher current densities the Tafel slopes increased up to ~ 60 mV dec^{-1}. The overpotential at the current density at j = -0.01 A cm^{-2} varied from 25 mV to 36 mV in acid solution, while being a slightly higher in alkaline electrolyte. These novel catalysts exhibited excellent activity, especially under industrial operating conditions of hydrogen evolution (j = -0.3 A cm-2) - the overpotentials for the best samples were ~ 70 mV only. The facts that electrodeposition is considered as cost effective synthesis way, as well as low cost and well established Ti$_2$AlC support preparation, these novel catalysts could be promising for commercial hydrogen production by water electrolysis.

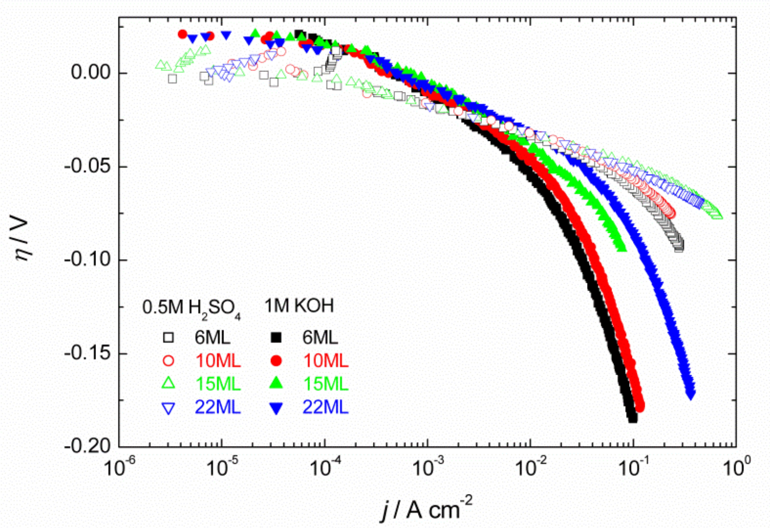

Fig1. HER polarization curves for representative Ir/Ti$_2$AlC samples in acid and alkaline electrolytes (ML-monolayer of iridium)

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Water Structure in the Sub-Membrane Region of a Floating Lipid Bilayer - the Effect of an Ion-Channel Formation and the Channel Blocker

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The structure of water in the sub-membrane region of the bilayer of DPhPC floating (fBLM) on a monolayer of 1-thio-β-D-glucose (β-Tg) modified gold nanoparticle film was studied by the surface enhanced infrared absorption spectroscopy (SEIRAS). SEIRAS employs surface enhancement of the mean square electric field of the photon which is acting on a few molecular layers above the film of gold nanoparticles. Therefore, it is uniquely suited to probe water molecules in the sub-membrane region and provides unique information concerning the structure of the hydrogen bond network of water surrounding the lipid bilayer. The IR spectra indicated that water with a strong hydrogen network is separating the membrane from the gold surface. This water is more ordered than water in the bulk. When alamethicin, a peptide forming ion channels is inserted into the membrane the network is only slightly loosened. The addition of amiloride-an ion channel blocker results in a significant decrease in the amount of water in the sub-membrane region. The remaining water has a significantly distorted hydrogen bonds network. This study provides unique information about the effect of the ion channel on water transport across the bilayer. The electrode potential has a relatively small effect on water structure in the sub-membrane region. However, the IR studies demonstrated that water is less ordered at positive transmembrane potentials. The present results provide significant insight into the nature of hydration of floating lipid bilayer on the gold electrode surface.

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"Water structure in the sub-membrane region of a floating lipid bilayer without and with an ion-channel and an ion channel blocker", ***Langmuir,*** **2020,***36*,404-418.

Interface Design for High Current Density Cycling of Solid State Batteries

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Solid-state batteries with Li metal anodes are emerging as a promising technology in the field of electrochemical energy storage, offering improved safety and high energy densities capable of meeting the demands of next-generation electric vehicles. Solid electrolytes based on doped, cubic $Li_7La_3Zr_2O_{12}$ (LLZO) garnets are a particularly promising class of materials for all-solid-state-batteries due to their wide electrochemical stability window and high Li-ion conductivities of ~1.0 mS cm−1 at 25ºC [1]. To realize their potential, tremendous efforts have been dedicated to improving the Li/garnet interface and increasing the critical current density at which failure takes place. With existing understanding of the surface chemistry of garnet pellets, specifically, the formation of Li2CO3 leading to increases in the Li/garnet interfacial impedance, various approaches have been developed to reduce, if not completely remove, the surface Li_2CO_3 layer [2]. In addition, maintaining uniform contact between Li metal and the solid electrolyte has also been shown to enable efficient, long-term plating and stripping of Li, as contact losses associated with morphological instabilities (e.g., vacancy accumulation and pore formation) are commonly found to be responsible for an increase in interfacial impedance and eventual cell failure [3]. Applied strategies have only managed to increase the cycle life of symmetric cells, and, until very recently, current densities above 1 mA cm-2 at 25ºC have remained inaccessible for planar LLZO membranes.

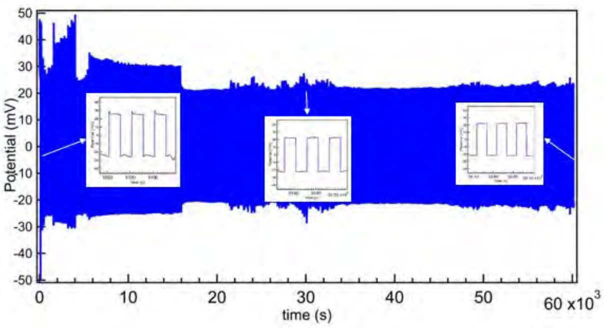

Figure 1. Galvanostatic cycling of Al-doped LLZO at 4 mA cm^{-2}. Al-doped LLZO sample exhibited stable DC cycling behavior for 18 h during 320 cycles.

Through the systematic application of our interfacial design strategy, we have demonstrated how deep understanding of the relationship between electrochemical performance of the anode-solid electrolyte interface and its structural and chemical properties can yield significant improvements in solid-state battery performance. Symmetric Li-Li coin cells were made using dense Al- and Ta-doped LLZO pellets prepared via our interface design strategy, which enabled cycling at current densities as high as 4 mA cm-2 without failure for >300 cycles with 0.5 µm Li plated/stripped per cycle. The significant improvements in performance demonstrated for both Ta- and Al-doped LLZO can be rationalized based on the combination of a conformal Li layer formed by vacuum deposition and complete formation of the ODI in the absence of any extrinsic oxide/carbonate impurities at the Li-LLZO interface. The presence of these features likely leads to a more homogeneous distribution of current density, inhibiting the nucleation of Li dendrites at so-called "hot spots," as well as the formation of a complete, self-limited reaction layer at the Li-LLZO interface. These results open up new opportunities to increase current densities in Li metal/solid electrolyte systems and approach performance limits that are dictated only by intrinsic materials properties.

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Copper (II) oxide Nanostructures Prepared by Dip Coating for Hydrogen Production via Photocatalytic Water Splitting

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Abstract

Copper (II) oxide (CuO) nanostructures were prepared on FTO using the sol-gel dip coating method. Two (2), four (4), six (6), eight (8) and ten (10) layers of dip coated films were prepared by drying each layer using a two-step method; at 110°C and 250°C for 10 and 5 min respectively. The films prepared were annealed at 550°C for 1 hr and allowed to cool down naturally to room temperature. The properties and photocatalytic performance of the films when applied towards hydrogen production were investigated. The XRD pattern of the films confirmed the tenorite phase of pure CuO. Raman spectroscopy only revealed the $1A_g$ and $2B_g$ phonon modes of CuO further confirming the purity of films produced. The photocatalytic performance of CuO films consisting of 6 layers produced the best results yielding photocurrent of -2.0 mA/cm^2 at -0.55 V vs Ag/AgCl while films with 2 layers recorded the least value of -1.1 mA/cm^2 at the same reference potential. Films prepared with 6 layers appeared to be more porous compared to others as revealed by FE-SEM studies, allowing for easier charge separation of photogenerated charge carriers, leading to the improved photocurrent observed. EIS analysis revealed the least charge transfer resistance at the CuO/electrolyte interface for films consisting of 6 layers while those with 2 yielded the highest values correlating with their photocatalytic performance. The two-step drying method for preparing CuO nanostructures have been optimized in this work, showing great promise for photocatalytic water splitting.

Keywords: Copper (II) oxide, dip coating, hydrogen production, photocatalysis

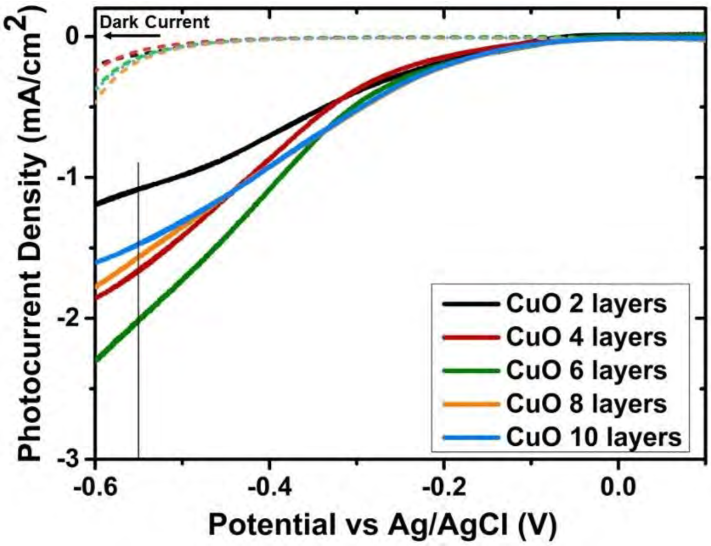

Figure 1. Photocurrent densities of nanostructured CuO films prepared by dip coating technique.