Program of the

17th Topical Meeting of the International Society of Electrochemistry

Multiscale Analysis of Electrochemical Systems

31 May - 3 June 2015
Saint-Malo, France

Organized by:
Division 4 Electrochemical Material Science
Division 7 Physical Electrochemistry
ISE Region France

International Society of Electrochemistry
Chemin du Closelet 2
1006 Lausanne
Switzerland

Copyright © 2015

All rights reserved. No part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.
No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of product liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

Printed in France

Organizing Committee

Philippe Hapiot, *Rennes, France*

Carlos M. Muller, *Barcelona, Spain*

Renat Nazmutdinov, *Kazan, Russia*

Nadine Pébère, *Toulouse, France* **(Chair)**

Monica Santamaria, *Palermo, Italy*

Maria Elena Vela, *La Plata, Argentina*

Table of Contents

Oral presentation program

Poster presentation program

Monday 18:10 to 19:30
Session 1

Tuesday 10:10 to 11:10
Session 2

Sunday, 31 May 2015

18:00 – 20:00

Welcome Reception
Room: Rotonde Jacques Cartier

Monday, 1 June 2015

08:30 - 08:50

Opening Ceremony
Room: Auditorium Chateaubriand

Monday, 1 June 2015, Morning

Keynote

Room: Auditorium

Chaired by: Christian Amatore

08:50 to 09:40 Keynote

Zhong-Qun Tian *(College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China)*

In-Situ Surface Enhanced Raman Spectroscopic Studies on Electrochemical Interfaces: From Molecular Intermediates to Surface Morphology

s1c: Development; Simulation and modelling (computational physical chemistry)

Room: Auditorium

Chaired by: Bernard Tribollet and Hiromitsu Takaba

09:50 to 10:10 Invited

Akos Kriston *(Institute for Energy and Transport, European Commission, DG Joint Research Center, Petten, the Netherlands)*, Lois Boon-Brett, Andreas Pfrang

Calculation of effective transport and kinetic parameters of electrochemical energy conversion and storage devices at multiple length scales

10:10 to 10:30

Timo Danner *(Department of Electrochemical Multiphysics Modeling, Helmholtz-Institute Ulm for Electrochemical Energy Storage, Ulm, Germany)*, Birger Horstmann, Arnulf Latz, Volker Schulz

Multiscale simulation of transport processes in metal-oxygen batteries

10:30 to 11:00 Coffee Break

11:00 to 11:20

Geonhui Gwak *(Mechanical Engineering, Inha University, Incheon, Korea)*

Three-dimensional transient modeling of non-aqueous electrolyte lithium-air battery

11:20 to 11:40

Trong-Khoa Nguyen *(Laboratoire de Réactivité et Chimie des Solides, Centre National de la Recherche Scientifique, Amiens, France)*, Alejandro A. Franco, Abdelouahab El Kharbachi, Dominique Larcher, Matias Quiroga, Kan-Hao Xue

Investigating transient phenomena in lithium ion batteries: A multiscale modeling approach

11:40 to 12:00

Manuelle Quinaud *(Liten, Cea, Grenoble, France)*, Federico Calle-Vallejo, Rodrigo Ferreira de Morais, Mathias Gerard, David Loffreda, Pascal Schott

Multiscale Modeling of PEMFC: From Atomistic Calculations to Cell Performance and Degradation

12:00 to 12:20

Carlos Ziebert *(IAM-AWP, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany)*, Boxia Lei, Andreas Melcher, Anna Ossipova, Magnus Rohde, Hans Jürgen Seifert

Multiscale electrochemical-thermal modeling of cylindrical Li-ion cells and comparison with electrochemical-calorimetric studies

s2e: Applications; Nanostructured materials

Room: Salle Bouvet

Chaired by: Philippe Hapiot and Monica Santamaria

09:50 to 10:10 Invited

Corinne Lagrost *(Institut des Sciences Chimiques de Rennes, CNRS and Université de Rennes 1, Rennes, France),* Nicolas Vandencasteele, Philippe Hapiot, Ivan Jabin, Yann Leroux, Sébastien Lhenry, Alice Mattiuzzi, Olivia Reinaud, Luis Santos

Electrografting at the Molecular Scale

10:10 to 10:30

Fetah Podvorica *(ITODYS, University Paris-Diderot, Paris, France),* Catherine Combellas, Dardan Hetemi, Frederic Kanoufi, Jean Pinson

Electrografting of Alkyl Films at Low Driving Force by Diverting the Reactivity of Aryl Radicals Derived from Diazonium Salts

10:30 to 11:00

Coffee Break

11:00 to 11:20 Invited

Yuri Pleskov *(Physical Electrochemistry, Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia),* Evgenii Ekimov, Valerii Elkin, Marina Krotova

Electrochemical Behaviour of Boron-doped Diamond Compacts - A New Electrode Material

11:20 to 11:40

Damaris Fernandez *(School of Chemistry & CRANN/AMBER, Trinity College Dublin, Dublin, Ireland),* Michael E.G. Lyons, Luis Romeral

The role of surface/volume ratio on electrochemical phase transformation reactions taking place at nano/micro-structured electrodes

11:40 to 12:00

Joanna Jalkh *(Equipe MaCSE, Institut des Sciences Chimiques, Rennes, France),* Philippe Hapiot, Corinne Lagrost, Yann Leroux

Comparative Electrochemical Investigations in Ionic Liquids and Molecular Solvents of a Carbon Surface Modified by a Redox Monolayer

12:00 to 12:20

Ioan Baldea *(Theoretische Chemie, Universität Heidelberg, Heidelberg, Germany)*

Unprecedented Efficiency to Simultaneously Control Orbital Energies and Vibrational Properties of Single-Molecule Junctions in Electrochemical Environment

Monday, 1 June 2015, Afternoon

s1c: Development; Simulation and modelling (computational physical chemistry)

Room: Auditorium

Chaired by: Mark Orazem and Akos Kriston

14:00 to 14:20

Hiromitsu Takaba *(Department of Environmental and Energy Chemistry, Kogakuin University, Tokyo, Japan)*, Md. Khorshed Alam

Multiscale Modeling of Degradation of Pt-Ru Alloy Particles for Anode Catalyst in PEFC Fuel Cell

14:20 to 14:40

Simon Hein *(Department of Computational Electrochemistry, German Aerospace Center, Stuttgart, Germany)*, Arnulf Latz

Influence of local lithium metal deposition in 3D microstructures on local and global behavior of Lithium-ion batteries

14:40 to 15:00

Kudakwashe Chayambuka *(Separation and Conversion Technology, VITO, Mol, Belgium)*, Xochitl Dominguez-Benetton

Multiscale Modelling of Porous Electrodes in Semi-solid Flow Batteries

15:00 to 15:20 Invited

Cristiana Di Valentin *(Materials Science Department, University of Milano Bicocca, Milano, Italy)*

Computational Electrocatalysis: Novel Materials For Oxygen Reduction Reaction (ORR) and Methanol Oxidation Reaction (MOR)

15:20 to 15:40

Wolfgang Schmickler *(Institute of Theoretical Chemistry, Ulm University, Ulm, Germany)*, Aleksej Goduljan, Leila Mohammadzadeh, Paola Quaino, Elizabeth Santos

Ions in Nanopores – Combining DFT with an Effective Hamiltonian Approach

15:40 to 16:00

Christian Merdon *(Numerical Mathematics and Scientific Computing, Weierstrass Institute for Applied Analysis and Stochastics, Berlin, Germany),* Helmut Baltruschat, Jürgen Fuhrmann, Mehdi Khodayari, Alexander Linke, Timo Streckenbach

Inverse modeling of thin layer flow cells for detection of solubility, transport and reaction coefficients from experimental data

16:00 to 16:30 Coffee Break

Chaired by: Wolfgang Schmickler and Cristiana Di Valentin

16:30 to 16:50 Invited

Mark E. Orazem *(Department of Chemical Engineering, University of Florida, Gainesville, USA),* Christopher L. Alexander, Bernard Tribollet

Influence of Micrometric-Scale Electrode Heterogeneity on Electrochemical Impedance Spectroscopy

16:50 to 17:10

Kyeongmin Oh *(School of Mechanical Engineering, Inha University, Incheon, Korea),* Hyunchul Ju, Seongyeon Won

Numerical analysis of vanadium and water crossover effects in all-vanadium redox flow batteries

17:10 to 17:30

Jean-Sébastien Filhol *(Institut Charles Gerhardt, Université de Montpellier, Montpellier, France)*, Nicolas Lespes

Ab Initio Modeling of the Solvent-Metal Electrochemical Interface

17:30 to 17:50

Wataru Yamamoto *(Environmental and Energy Chemistry, Kogakuin University, Hachioji, Japan)*, Hiromitsu Takaba

Analytical Study of Polarization Curve of Li-Air Battery based on Novel Products Deposition Model Suggested by First-principles Molecular Dynamics Simulations

17:50 to 18:10

Pierre-Yves Olu *(LEPMI, Grenoble-INP, St Martin d'Heres, France),* Antoine Bonnefont, Sébastien Bozdech, Marian Chatenet, Nathalie Job, Marlène Rouhet, Elena Savinova

Dual role of hydroxide adsorption for borohydride electrooxidation reaction on Platinum

s2e: Applications; Nanostructured materials

Room: Salle Bouvet

Chaired by: Maria Elena Vela and Yu Pleskov

14:00 to 14:20 Invited

Cesar Alfredo Barbero *(Chemistry, National University of Rio Cuarto, Rio Cuarto, Argentina)*, Angelica Baena Moncada, Paula Cappellari, Rusbel Coneo Rodriguez, Gonzalo Garcia, Elena Pastor, Gabriel Planes

Hierarchical Nanostructured Fuel Cell Electrodes Studied by *In-situ* Electrochemical Techniques

14:20 to 14:40

Elizabeth Santos *(Institute of Theoretical Chemistry, Ulm University, Ulm, Germany),* Leandro Moreira de Campos Pinto, Paola Quaino

Local reactivity at Pd nanoclusters

14:40 to 15:00

Monica Santamaria *(DICAM, Università di Palermo, Palermo, Italy),* Francesco Di Franco, Francesco Di Quarto, Hiroki Habazaki, Andrea Zaffora

Photoelectrochemical evidence of inhomogeneous composition at nm length scale of anodic films on valve metals alloys

15:00 to 15:20

Gourav Singla *(School of Physics and Materials Science, Thapar University, Patiala, India)*

Structural, thermal and electrochemical study of single step synthesized WC nanopowder

s2c: Applications; Electrochemistry in biological systems

Room: Salle Bouvet

Chaired by: Maria Elena Vela and Yu Pleskov

15:20 to 15:40 Invited

Sophie Griveau *(Unité de Technologies Chimiques et Biologiques pour la Santé, Chimie ParisTech - ENSCP, Paris, France),* Abdelilah Amar, Fethi Bedioui, Fatemeh Razzaghi, Johanne Seguin

Scanning electrochemical microscopy imagery of living tumoral cells at constant height

15:40 to 16:00 Invited

Manuela Rueda *(Physical Chemistry, University of Seville, Seville, Spain)*, Julia Alvarez-Malmagro, Francisco Prieto

Adenine-Thymine Co-adsorption at Gold Electrodes as a Function of pH: An *in-situ* FT-IR Spectro-electrochemical Study

16:00 to 16:30 Coffee Break

Chaired by: Manuela Rueda and Sophie Griveau

16:30 to 16:50

Ezat Hamidi-Asl *(AXES Research Group, Department of Chemistry, University of Antwerp, Antwerp, Belgium)*, Devin Daems, Karolien De Wael, Luc J. Nagels, Guy Van Camp

Determination of the Association Constant Between Small Target Molecules and Large Biomolecules by Potentiometric Titration

16:50 to 17:10

Lourdes Mónica Bravo Anaya *(Departamento de Ingeniería Química, Universidad de Guadalajara, Guadalajara, Mexico)*, Norberto Casillas, Erika Roxana Larios Durán, Yahya Rharbi, J.F. Armando Soltero

Thermodynamic Study of the Adsorption of Calf Thymus DNA at the Platinum/Buffer Electrolyte Interface

17:10 to 17:30 Invited

Manon Guille-Collignon *(UMR 8640 Chemistry Dept. ENS PSL, UPMC Sorbonne Universités, Paris, France)*, Christian Amatore, Rémy Fulcrand, Frédéric Lemaître, Yun Li, Anne Meunier, Catherine Sella, Laurent Thouin

Microsystems for Oxidative Stress Species Electrochemical Detection at the Level of a Cellular Population

17:30 to 17:50

Tomas Navratil *(Department of Biomimetic Electrochemistry, J. Heyrovský Institute of Physical Chemistry of the AS CR, Prague, Czech Republic),* Jana Jaklova Dytrtova, Jan Langmaier, Katerina Novakova, Ivana Sestakova, Romana Sokolova

Biomimetic Membranes and Characterization of Transport of Biochemically Important Species across them

18:10 to 19:30

Poster Session 1

Room: Grand Large

Tuesday, 2 June 2015, Morning

Keynote

Room: Auditorium

Chaired by: Mark E. Orazem

08:30 to 09:20 Keynote

Richard Compton *(Department of Chemistry, Oxford University, Oxford, United Kingdom)*

Electrochemical studies of nanoparticles

s1a: Development; SECM, LEIS

Room: Auditorium

Chaired by: Annick Hubin and Vincent Vivier

09:30 to 09:50 Invited

Mathieu Etienne *(LCPME, CNRS and Université de Lorraine, Villers-lès-Nancy, France)*

Scanning electrochemical microscopy with shearforce detection: Some examples of application

09:50 to 10:10

Vasilica Badets *(NSYSA, University of Bordeaux, Institut des Sciences Moleculaires, Bordeaux, France),* Olivier Fontaine, Damien Quinton, Dodzi Zigah

SECM Writing and Reading with an Original Dual Microelectrode

10:10 to 11:10

Poster Session 2
Room: Grand Large

11:10 to 11:30

Wolfgang Schuhmann *(Analytical Chemistry - Center for Electrochemical Sciences, Ruhr-Universität Bochum, Bochum, Germany)*, Alexander Botz, Justus Masa, Michaela Nebel, Daniela Wintrich

SECM meets electrocatalysis

11:30 to 11:50

Mike O'Connell *(Materials, National Physical Laboratory, Teddington, United Kingdom)*, Andy Wain

Mapping Oxygen Reduction at Nanostructured Catalysts: From Ensembles to Individual Particles

11:50 to 12:10

Yann Leroux *(Institut des Sciences Chimiques de Rennes, CNRS - Université de Rennes 1, Rennes Cedex, France)*, Francoise Conan, Nathalie Cosquer, Philippe Hapiot, Yves Le Mest, Nicolas Le Poul, Sébastien Lhenry, Christophe Orain, Olivia Reinaud

Locally self-induced "electro-click" onto self-assembled monolayer: Evidence for surface self-catalysis propagation

12:10 to 12:30

Gunther Wittstock *(Department of Chemistry, Carl von Osseitzky University of Oldenburg, Oldenburg, Germany)*, Heinz Bülter, Fabian Peters, Inka Plettenberg, Patrick Schwager, Julian Schwenzel

Scanning elctrochemical microscopy of interfaces in lithium-ion and metal-air batteries

s2a: Applications; Materials for energy; synthesis and characterization

Room: Salle Bouvet

Chaired by: F. Javier Recio and Vitali Grozovski

09:30 to 09:50

Steven Le Vot *(IRAMIS, NIMBE (UMR 3685), LICSEN, CEA Saclay, Saclay, France)*, Bruno Jousselme, Guillaume Laffay

Electrochemical and Physico-Chemical Investigation of New Promising N-Functionalized Carbon Nanotubes for Oxygen Reduction Reaction

09:50 to 10:10

Oc Hee Han *(Western Seoul Center, Korea Basic Science Institute, Seoul, Korea)*

Chemical Structure and Dynamics of Functional Materials for Electrochemical Systems Investigated by Nuclear Magnetic Resonance Spectroscopy

10:10 to 11:10

Poster Session 2
Room: Grand Large

11:10 to 11:30

Vitali Grozovski *(Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland)*, Akiyoshi Kuzume, Enn Lust, Ilya Pobelov, Tavo Romann

In-situ AFM Studies of Hydration Effect at Sputtered Iridium Dioxide Thin Films

11:30 to 11:50

Jeremy Come *(Center for Nanophase and Materials Science, Oak Ridge National Laboratory, Oak Ridge, USA),* Nina Balke, Majid Beidaghi, Jennifer Black, Yury Gogotsi, Sergei Kalinin, Maria Lukatskaya, Michael Naguib

Probing the Mechanical Deformation of 2D Metal Carbides upon Cation Intercalation at the Nanoscale

11:50 to 12:10 Invited

Bing Joe Hwang *(Department of Chem. Eng., National Taiwan University of Science and Technology, Taipei, Taiwan)*, Van Thi Thanh Ho, Jyh-Fu Lee, Trung-Thanh Nguyen, Chun-Jern Pan, Hwo-Shuenn Sheu, Wei-Nien Su, Mon-Che Tsai

Synthesis and Characterization of Novel $Pt/Ti_xM_{1-x}O_2$ Nanocatalysts

12:10 to 12:30

Tso-Fu Mark Chang *(Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Japan)*, Chun-Yi Chen, Yung-Jung Hsu, Wei-Hao Lin, Tatsuo Sato, Masato Sone

Effect of Pressure on Titanium Dioxide Electrodeposited Cathodically with Supercritical Carbon Dioxide

Tuesday 2, June 2015, Afternoon

s1a: Development; SECM, LEIS

Room: Auditorium

Chaired by: Francesco Di Quarto and Hiroki Habazaki

14:00 to 14:20

Renaud Cornut *(IRAMIS/NIMBE/LICSEN, CEA, Gif-sur-Yvette, France)*, Michael Bertucchi, Tiphaine Bourgeteau, Stephane Campidelli, Vincent Derycke, Bruno Jousselme, Steven Le-Vot

New insights in the electronic transport in reduced graphene oxide using Scanning Electrochemical Microscopy

14:20 to 14:40 Invited

Vincent Vivier *(Laboratoire Interfaces et Systèmes Electrochimiques, CNRS - UPMC, Paris, France)*, Michel Keddam, Christel Laberty-Robert, Beatriz Puga, Carlos M. Sánchez-Sánchez

Local photoelectrochemical characterization of semi-conducting materials for water splitting

14:40 to 15:00 Invited

Ricardo M. Souto *(Department of Chemistry, University of La Laguna, La Laguna (Tenerife), Spain)*, Javier Izquierdo

Possibilities and Limitations of Scanning Electrochemical Microscopy for the Investigation of Corrosion Mechanisms

15:00 to 15:20 Invited

Annick Hubin *(Electrochemical and Surface Engineering, Vrije Universiteit Brussel, Brussels, Belgium)*, Sara Bals, Diederik Depla, Thibault Muselle

AFM-LEIS for local electrochemical characterization

15:20 to 15:40

Olivier Devos *(I2M, I2M, Talence, France)*, Emilie Bousquet, Mohamed El May, Thierry Palin-Luc, Angeline Poulon-Quintin, Monique Puiggali, Nicolas Saintier, Djoudi Sidane, Marie Touzet, Vincent Vivier

Comparison between SECM and LEIS measurements in the study of FSW alloy assembly

15:40 to 16:00

Nicolas Murer *(Products/Marketing, Bio-Logic SAS, Claix, France),* Samantha Catarelli, John Griffiths, Daniel Lonsdale

Using intermittent contact (ic) SECM for corrosion and energy storage materials investigation

16:00 to 16:20 Invited

Christine Kranz *(Institute of Analytical and Bioanalytical Chemistry, University of Ulm, Ulm, Germany)*, Alexander Eifert, Javier Izquierdo, Ricardo M. Souto

Combined AFM-SECM for corrosion studies

s2f: Applications; Corrosion and protection

16:20 to 16:40

Andrej Nazarov *(Electrochemistry, French Corrosion Institute, Brest, France)*, Nuria Casals, Dominique Thierry, Flavien Vucko

SKP and EIS Characterization of the passivity 301 Stainless Steel under Mechanical Stress

16:40 to 17:00

Coffee Break

Chaired by: Carlos Muller and Christine Kranz

17:00 to 17:20 Invited

Michele Curioni *(Corrosion and Protection Centre, School of Materials, University of Manchester, Manchester, United Kingdom)*

Looking Closely at Magnesium Corrosion: Electrochemical Methods, Real-time Optical Imaging and Hydrogen Measurement

17:20 to 17:40

Francesco Di Quarto *(DICAM, Università di Palermo, Palermo, Italy),* Francesco Di Franco, Monica Santamaria

A Chemical Approach to the Modelling of Band Gap of Passive Films for Corrosion Studies

17:40 to 18:00

Marie Benoit *(LECNA, CEA Saclay, Gif-sur-Yvette, France)*, Christian Bataillon, Benoit Gwinner, Frédéric Miserque, Carlos M. Sánchez-Sánchez, Bernard Tribollet, Vincent Vivier

Influence of a passive layer on the kinetics of an electron transfer reaction

18:00 to 18:20

Lijing Yang *(Chinese Academy of Sciences, Ningbo Institute of Material Technology & Engineering, Ningbo, China)*

Electrochemical corrosion behavior of S32750 super duplex stainless steel in NaCl solution

18:20 to 18:40

Ronald Clark *(Materials Research Centre, College of Engineering, Swansea University, Swansea, United Kingdom)*, Steve Walters, Geraint Williams

A Scanning Probe Investigation of Inter-Granular Corrosion in Sensitized Stainless Steel Nuclear Fuel Cladding

20:00 to 23:00

Cocktail and Banquet

Room: Rotonde Jacques Cartier

s2d: Applications; Electrochemical sensors and biosensors

Room: Salle Bouvet

Chaired by: Richard Compton and Paul Kilmartin

14:00 to 14:20

Isabelle Mazerie *(Institute of Chemical Science of Rennes, University of Rennes 1, Rennes, France),* Idriss Bakas, Benjamin Carbonnier, Mohamed Mehdi Chehimi, Nathalie Coulon, Pierre Didier, Didier Floner, Florence Geneste, Aurélie Girard, Florence Razan

Design of Portable Sensor to Detect Hazardous Molecules in our Environment

14:20 to 14:40

Miroslav Fojta *(Department of Biophysical Chemistry and Molecular Oncology, Institute of Biophysics, ASCR, v.v.i., Brno, Czech Republic),* Ludek Havran, Iva Kejnovska, Hana Pivonkova, Libuse Trnkova, Pavlina Vidlakova, Michaela Vorlickova

Behavior of G-Quadruplex Forming DNA Oligonucleotides at Electrically Charged Surfaces of Mercury and Carbon Electrodes

14:40 to 15:00

Aihua Liu *(Laboratory for Biosensing, Qingdao Institute of Bioenergy & Bioprocess Technol, CAS, Qingdao, China)*, Lei Han, Shu Zhang

Novel glucose sensor based on electrocatalytic reduction of hydrogen peroxide at Au@Ag heterogeneous nanorods

15:00 to 15:20

Kristina Tschulik *(Chemistry, University of Oxford, Oxford, United Kingdom)*, Richard Compton

Electrochemical Sizing and Detection of Magnetic Field-induced Agglomeration of Individual Fe_3O_4 Nanoparticles

15:20 to 15:40

Paul Kilmartin *(School of Chemical Sciences, University of Auckland, Auckland, New Zealand)*, Hande Karaosmanoglu, Alexander Turke, Qiang Zhang

PEDOT Electrochemical Sensors using Macro and Micro-Electrodes

15:40 to 16:00

Jiri Barek *(Department of Analytical Chemistry, Faculty of Science, Charles University in Prague, Prague, Czech Republic)*

Voltammetric and Amperometric Monitoring of Biomarkers using Non-Traditional Electrode Materials and Arrangements

16:00 to 16:20 Invited

Conor Hogan *(Department of Chemistry and Physics, La Trobe University, Melbourne, Australia)*, Paul S. Francis

New Dimensions in Electrochemiluminescence Sensing

16:20 to 16:40

Jan Clausmeyer (*Analytische Chemie – Center for Electrochemical Sciences, Ruhr-Universität Bochum, Bochum, Germany)*, Paolo Actis, Babak Babakinejad, Yuri Korchev, Ainara López Córdoba, Miriam Marquitan, Wolfgang Schuhmann, Yanjun Zhang

Carbon Nanoelectrodes for Single-Cell Analysis: From Amperometric Sensing to Field-Effect Transistors

16:40 to 17:00

Coffee Break

s2b: Applications; Energy conversion and storage

Chaired by: Carlos Ziebert and Ladislav Kavan

17:00 to 17:20

Ken-Ming Yin *(Chemical Engineering, Yuan Ze University, Chung Li, Taiwan)*

Agglomerate Catalyst Layer Model on the Membrane Electrode Assembly of Proton Exchange Membrane Fuel Cell

17:20 to 17:40

Jean-Marc Noel *(Laboratoire ITODYS UMR 7086 CNRS, University of Paris Diderot, Paris, France)*, Catherine Combellas, Frederic Kanoufi, Anna Proust, Florence Volatron

Electronic and Catalytic Properties of Hybrid Polyoxometalates Layer Grafted on Conductive and Semiconductive Substrates

17:40 to 18:00

Andebet Gedamu Tamirat *(Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan)*, Amare Aregahegn Dubale, Wei-Nien Su, Hung-Ming Chen, Bing Joe Hwang

Photoelectrochemical Water Splitting at Low Applied Potential Using NiOOH Coated Codoped (Sn, Zr) α-Fe_2O_3 Photoanode

18:00 to 18:20

Ladislav Kavan *(Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic)*, Shaik M. Zakeeruddin, Michael Graetzel, Paul Liska

Efficient FTO-Free Cathode for Dye-sensitized Solar Cells

18:20 to 18:40

Fu-Ming Wang *(Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, Taiwan)*

In-operando electrochemical-surface plasma resonance (EC-SPR) observation to the kinetic study of solid electrolyte interface (SEI) formation on lithium ion battery

20:00 to 23:00

Cocktail and Banquet

Room: Rotonde Jacques Cartier

Wednesday, 3 June 2015, Morning

s1b: Development; Advanced techniques for surface characterization

Room: Lamennais 1/2

Chaired by: Zhong-Qun Tian and Maria Elena Vela

08:30 to 08:50 Invited

Frederic Kanoufi *(ITODYS UMR7086, Université Paris Diderot - CNRS, Paris, France)*, Christopher Batchelor-McAuley, Catherine Combellas, Richard Compton, Ariadna Martinez-Marrades, Anisha N. Patel, Gilles Tessier, Kristina Tschulik

Monitoring the Reactivity of Individual Ag Nanoparticles by High Resolution Optical Microscopy and Electrochemistry

08:50 to 09:10

Lukasz Poltorak *(LCPME, Université de Lorraine, Nancy, France),* Manuel Dossot, Grégoire Herzog, Alain Walcarius

Local characterization by confocal Raman spectroscopy and scanning electrochemical microscopy of liquid/liquid micro-interfaces modified with mesoporous silica

09:10 to 09:30

Fabio La Mantia *(Analytical Chemistry, Ruhr-Universität Bochum, Bochum, Germany)*, Andjela Petkovic

Nonlinear behavior of the electron-transfer process

09:30 to 09:50 Invited

Manuel M. Lohrengel *(Physical Chemistry and Electrochemistry, Heinrich-Heine-University Dusseldorf, Dusseldorf, Germany)*, Kamil P. Rataj, Christoph Schnitter

Electrochemical Machining - Shaping by Anodic Dissolution

09:50 to 10:10

Michal Manko *(Institut fuer Physikalische Chemie II, Heinrich-Heine-Universitaet Duesseldorf, Duesseldorf, Germany),* Manuel Lohrengel, Kamil P. Rataj, Christoph Schnitter

Tantalum nanoparticles for electrolytic capacitors

10:10 to 10:30

Coffee Break

s1c: Development; Simulation and modelling (computational physical chemistry)

Chaired by: Bernard Tribollet and Timo Danner

10:30 to 10:50

Jürgen Fuhrmann *(Numerical Mathematics and Scientific Computing, Weierstrass Institute, Berlin, Germany)*, Christian Merdon

A numerical method for Nernst-Planck-Poisson Systems with volume constraints

10:50 to 11:10

Jouke Dykstra *(Sub-department of Environmental Technology, Wageningen University, Wageningen, the Netherlands)*, Maarten Biesheuvel, Albert van der Wal

Combined EDL and transport modeling in water desalination

11:10 to 11:30

Christoffer Nielsen *(Department of Physics, Technical University of Denmark, Kongens Lyngby, Denmark)*, Henrik Bruus

Sharp-interface model of electrodeposition and dendritic growth

s2b: Applications; Energy conversion and storage

Chaired by: Bernard Tribollet and Timo Danner

11:30 to 11:50

François Astier *(Electrochemical Engineering, South Brittany University, Lorient, France)*

Experimental Study of Small Lead Acid Batteries Regeneration Performance Modelling in Time

11:50 to 12:10

Sergey Grigoriev *(Chemistry and Electrochemical Power Engineering, National Research University Moscow Power Engineering Institute, Moscow, Russia),* Vladimir Fateev, Valery Kalinichenko, Irina Maruseva, Pierre Millet, Artem Pushkarev

Development and characterization of electrocatalytic layers based on reduced graphene oxide for PEM fuel cell applications

12:10 to 12:30

Christopher Charton *(CEA, Monts, France)*, Agnès Biller, Hervé Galiano, Matthieu Le Digabel, Daniel Lemordant, Jesus Santos Peña

"High Voltage" Li-ion Batteries Electrolyte Formulation for Stable Interfaces

14:00 to 20:00

Excursion to Mont Saint Michel

---

s2a: Applications; Materials for energy; synthesis and characterization

Room: Lamennais 4/5

Chaired by: Bing Joe Hwang and Tomas Mikysek

08:30 to 08:50

Amare Aregahegn Dubale *(Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan)*, Wei-Nien Su, Hung-Ming Chen, Bing Joe Hwang, Chun-Jern Pan, Andebet Gedamu Tamirat

Nickel decorated Cu_2O/CuO as a highly efficient photocathode for photoelectrochemical water reduction

08:50 to 09:10

Karina Elumeeva *(Analytical Chemistry - Center for Electrochemical Sciences, Ruhr-Universität Bochum, Bochum, Germany)*, Justus Masa, Wolfgang Schuhmann, Frank Tietz

A simple approach towards high-performance perovskite-based bifunctional oxygen electrocatalysts

09:10 to 09:30

Mitsuharu Chisaka *(Department of Electronics and Information Technology, Hirosaki University, Hirosaki, Japan)*, Noriaki Itagaki, Hirokazu Muramoto, Hirohito Sasaki

Evaluation of the oxygen reduction reaction activity of nano-oxynitride catalysts with conventional electrochemical techniques

09:30 to 09:50

F. Javier Recio *(Departamento de Química de los Materiales, Universidad Santiago de Chile, Santiago de Chile, Chile)*, Carmen Castro, Nataly Silva, Federico Tasca, José H. Zagal, César Zúñiga

Catalytic activity of MN_4 complexes adsorbed on carbon nanotubes towards oxygen reduction

09:50 to 10:10

Francesco Carla *(ESRF, The European Synchrotron, Grenoble, France)*

Understanding Electrochemical Layer by Layer Deposition: Order and Epitaxy in CdS Thin Films on Ag(111) Investigated by *In-situ* by Surface X-ray Diffraction

10:10 to 10:30

Coffee Break

Chaired by: Michele Curioni and Nadine Pébère

10:30 to 10:50

Tomáš Mikysek *(Department of Analytical Chemistry, University of Pardubice, Pardubice, Czech Republic)*, Jirí Ludvík

Electrochemical Characterization of Various Diketopyrrolopyrrole Derivatives with Respect to HOMO/LUMO Energies

10:50 to 11:10

Sylvie Genies *(Liten, Commissariat d'énergie atomique et aux énergies alternatives, Grenoble, France)*, Mélanie Alias, Adrien Boulineau, Isabel Jiménez Gordon, Viet-Phong Phan, Gregory Si Larbi

Implementation of Electrochemical Impedance Spectroscopy (EIS) in symmetric cells for evaluating the post-mortem protocols applied to characterize electrode materials in Li-ion batteries

s2f: Applications; Corrosion and protection

Chaired by: Michele Curioni and Nadine Pébère

11:10 to 11:30 Invited

Hiroki Habazaki *(Faculty of Engineering, Hokkaido University, Sapporo, Japan),* Yoshitaka Aoki, Achim W. Hassel, Taiki Kimura, Etsushi Tsuji, Takayoshi Yano

Characterization of Corrosion-resistant Aluminosilicate Coatings Prepared by Multiple Sol-Gel Spin Casting

11:30 to 11:50

Nathan Cooze *(College of Engineering, Swansea University, Swansea, United Kingdom)*, C. Gallagher, T. Lewis, T. Prosek, J.H. Sullivan, Dominique Thierry

A novel time-lapse microscopy technique to study the corrosion mechanisms and corrosion inhibitor effects during corrosion of Zinc Magnesium Aluminium (ZMA) alloys

11:50 to 12:10

Natalie Wint *(Materials Engineering, Swansea University, Swansea, United Kingdom)*, Arnoud deVooys, Steven Geary, Hamilton Neil McMurray

A Multi Length Scale Study of Cathodic Disbondment from Tin and Iron-Tin Intermetallic Coated Steel

12:10 to 12:30

Thi Xuan Hang To *(Laboratory for Protective Coatings, Institut de Technologie Tropicale, VAST, Hanoi, Viet Nam)*, Thi Mai Thanh Dinh, Tuan Anh Nguyen, Nadine Pebere, Hoang Thai, Anh Truc Trinh

Corrosion protection of a carbon steel by water based epoxy coatings containing hydrotalcite intercalated with molybdate

14:00 to 20:00

Excursion to Mont Saint Michel

Poster Presentations

Room: Salle du Grand Large

All posters will be on display from Monday 10:00 to Tuesday 17:00

Monday 18:10 to 19:30

Poster Presentation Session 1

Symposium 1a: Development; SECM, LEIS
Symposium 1b: Development; Advanced techniques for surface characterization
Symposium 1c: Development; Simulation and modelling (computational physical chemistry)
Symposium 2a: Applications; Materials for energy; synthesis and characterization
Symposium 2b: Applications; Energy conversion and storage

Tuesday 10:10 to 11:10

Poster Presentation Session 2

Symposium 2c: Applications; Electrochemistry in biological systems
Symposium 2d: Applications; Electrochemical sensors and biosensors
Symposium 2e: Applications; Nanostructured materials
Symposium 2f: Applications; Corrosion and protection

Session 1

Symposium 1a: Development; SECM, LEIS

s1a-001

Alexander Botz *(Analytical Chemistry - Center for Electrochemical Sciences, Ruhr-Universität Bochum, Bochum, Germany)*, Michaela Nebel, Wolfgang Schuhmann, Edgar Ventosa

Onset potential determination at gas-evolving catalysts by means of constant-distance mode positioning of nanoelectrodes

Symposium 1b: Development; Advanced techniques for surface characterization

s1b-001

Larbi Bait *(Centre de Développement des Technologies Avancées (CDTA), Université des sciences et technologie Houari Boumediène, Algiers, Algeria)*, Noureddine Madaoui, Nadia Saoula

Structural and Electrochemical Study of a coated stainless steel 304L by PVD method

s1b-002

Elena Binkauskiene *(Institute of Chemistry, Center for Physical Sciences and Technology, Vilnius, Lithuania)*, Virginijus Bukauskas, Vitalija Jasulaitiene, Albinas Lugauskas

The Studies of the Redox Behaviour of the Hydroquinone/Quinone Couple on Biologically Treated Polyaniline

s1b-003

Sang-Hyeon Ha *(Agency for Defense Development, Daejeon, Korea)*

A Multiscale image analysis for the electrolyte and stacking sequence of thermal activated batteries

s1b-004

Fabien Miomandre *(PPSM, ENS CACHAN, France)*, Jean-Frédéric Audibert, Jean-Christophe Lacroix, Pascal Martin, Clarisse Tourbillon

Combining SECM and fluorescence microscopy : A way to investigate electrochemically monitored luminescence on plasmonic electrodes

Symposium 1c: Development; Simulation and modelling (computational physical chemistry)

s1c-001

Zeno Farkas *(Department of Applied Analysis, Eötvös Loránd University, Budapest, Hungary)*, Istvan Farago, Akos Kriston

Development and mathematical analysis of operator splitting techniques applied to multiscale models of Li-ion batteries

s1c-002

Olga Gichan *(Theory of Nanostructured Systems, Chuiko Institute of Surface Chemistry, Kyiv, Ukraine)*, Valentina Pototskaya

Dynamic Instabilities at Electrified Interfaces of Different Geometry

s1c-003

Valeriy Kublanovsky *(Electrochemistry, Institute of General & Inorganic Chemistry, Kiev, Ukraine)*

The Electrochemically Active Complexes Formation in the Ion Discharge from Aqueous Electrolytes

s1c-004

Shruti Srivastav *(Department of Chemistry-Ångström Laboratory, Uppsala University, Uppsala, Sweden)*, Daniel Brandell, Kristina Edström, Chao Xu

Finite Element Modeling the Morphological Background to Capacity Fade in Si-based Lithium-Ion Batteries

Symposium 2a: Applications; Materials for energy; Synthesis and characterization

s2a-001

Mohamad Deraman *(School of Applied Physics, Faculty of Sciences & Technology, University Kebangsaan Malaysia, Bangi, Malaysia)*, R. Rarma, A. Awitdrus, N. H. Basri, W.M.H. Husin, M.R.M. Jasni, N.S.M. Nor, R. Omar, M.A.R. Othman, E. Taer, B. Yatim

Energy Storage Device Electrodes from Biomass Fibers and Biofilm

s2a-002

Freddy Escobar *(LISE, Université Pierre et Marie Curie, Paris, France),* Claude Gabrielli, Hubert Perrot, Ozlem Sel

A new approach towards understanding of the ion transfer dynamics in nanostructured carbon films for energy storage applications

s2a-003

Mathieu Etienne *(LCPME, CNRS and Université de Lorraine, Villers-lès-Nancy, France)*, Michel Perdicakis, Mateusz Donten, Cana Khalouche, Carole Lainé, Ievgen Mazurenko, Andreea Pasc, Ivan Vakulko, Alain Walcarius

Functional porous materials for redox flow batteries

s2a-004

Daniel Kimmich *(Department of Chemistry, Carl von Ossietzky Universität Oldenburg, Oldenburg, Germany),* Carsten Dosche, Gunther Wittstock

Photoelectrochemical screening of water splitting catalysts

s2a-005

Maria Luisa Lozano Camargo *(Ingeniería Ambiental, Tecnológico de Estudios Superiores del Oriente del Estado de México, Mexico),* Enrique Barrera Calva, Enrique Cañeda Guzmán, Erwin Said Guillen López, Arturo Nascir Pérez Martínez

Activated carbon obtained by bambu species of African oldhamii by physical activation for be used in air filters s2a-006

José Luis Mesa *(Química Inorgánica, Universidad del País Vasco, UPV/EHU, Leioa, Spain)*, Andrés T. Aguayo, María I. Arriortua, Miguel Bengoechea, Teresa Berrocal, J. Alberto Blázquez, Iratxe de Meatza, Edurne S. Larrea, Jesús Rodríguez-Fernández

Two Related Electrochemical Active Phosphites: $Li_{1.43}[Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO_3)_6]\bullet 1.5H_2O$ (1) and $Li_{0.86}[Fe^{II}_{3.86}Fe^{III}_{1.14}(HPO_3)_6]\bullet 0.8H_2O$ (2)

s2a-007

Walaa Nasseraldine *(Chemistry ICGM CMOS, University of Montpellier 2, Montpellier, France)*

How to understand oxygen reduction at porous electrodes in the aprotic lithium-air battery: Rotating ring disk investigation or scanning electrochemical microscopy?

s2a-008

Gumjae Park *(Battery Research Center, Korea Electrotechnology Research Institute, Changwon-si, Korea)*, Sang-Min Lee, Sungju Sim

Electrochemical properties of tin phosphide composite anode for sodium ion batteries

s2a-009

Arturo Nascir Pérez Martínez *(Ingeniería Ambiental, Tecnológico de Estudios Superiores del Oriente del Estado de México, Mexico)*, Enrique Barrera Calva, Enrique Cañeda Guzmán, Erwin Said Guillen López, Carlos David Hernpandez Pérez

Getting graphene from graphite deposited by commercial technique rocio pyrolitic

s2a-010

Jaroslav Stejskal *(Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic)*, Irina Sapurina, Miroslava Trchova

Polypyrrole Nanotubes with Noble-metal Nanoparticles and their Carbonized Analogues

s2a-011

Miroslava Trchova *(Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic)*, Michal Blaha, Zuzana Moravkova, Jaroslav Stejskal

Conducting Materials Prepared by the Oxidation of p-Phenylenediamine with p-Benzoquinone s2a-012

Lianqin Wang *(Istituto di Chimica dei Composti Organometallici, National Research Council, Sesto Fiorentino, Italy)*, Marco Bellini, Manuela Bevilacqua, Yanxin Chen, Jonathan Filippi, Alesandro Lavacchi, Andrea Marchionni, Hamish Miller, Francesco Vizza

Oxidation of Palladium: Nanoscale Effects in the Deactivation Toward Alcohols Electrooxidation

s2a-013

Chunman Zheng *(College of Aerospace Science and Engineering, National University of Defense Technology, Changsha, China)*, Yujie Li, Yong Liu, Yi Pan, Hui Wang, Kai Xie

The Analysis of Solid Electrolyte Interphase on Graphitic Anode

Symposium 2b: Applications; Energy conversion and storage

s2b-001

Yufang Chen *(College of aerospace science and engineering, National university of defense technology, Changsha, China)*, Yujie Li, Yi Pan, Kai Xie, Chunman Zheng

Influence of Co Content on Structure and Electrochemical Performance of $Li_{7/}6Mn_{1/2-x}Ni_{1/6}Co_{1/6+x}O_2$(x=0, 1/12, 1/6) as Cathode Materials

s2b-002

Jan Clausmeyer *(Analytische Chemie – Center for Electrochemical Sciences, Ruhr-Universität Bochum, Bochum, Germany)*, Justus Masa, Wolfgang Schuhmann

Electrocatalysis at the Nanoscale – Oxygen Evolution Reaction (OER) at Single Submicrometric $Ni(OH)_2$ Particles

s2b-003

Alberto Ganassin *(Chemistry, Ruhr-University Bochum, Bochum, Germany)*, Aliaksandr S. Bandarenka, Viktor Colic, Wolfgang Schuhmann, Jakub Tymoczko

Non-covalent Interactions in Water Electrolysis: Influence on the Activity of Pt(111) and Iridium Oxide Catalysts in Acidic Media

s2b-004

Irina Gocheva *(Mobility Department, Electric Drive Technology, AIT Austrian Institute of Technology, Vienna, Austria)*, Alfred Amon, Roman Binder, Wolfgang Marzinger, Erwin Rosenberg, Atanaska Trifonova

Coupled FTIR-GC/MS for *in-situ* characterization of gas species emitted from lithium ion batteries

s2b-005

Sergey Grigoriev *(Chemistry and Electrochemical Power Engineering, National Research University Moscow Power Engineering Institute, Moscow, Russia)*, Dmitri Bessarabov, Alexander Kalinnikov, Jan Van Der Merwe

Mathematical modeling and experimental study of current distribution in PEM water electrolyser

s2b-006

Mok-Hwa Kim *(Department of Materials Science & Engineering, Yonsei University, Seoul, Korea)*, Joong Tark Han, Kisuk Kang, Kwang-Bum Kim, Kwang Chul Roh

Ribbon-like activated carbon with a multi-structure for supercapacitors

s2b-007

Jong Dae Lee *(Department of Chemical Engineering, Chungbuk National University, Cheongju, Korea)*, Ji Yong Park

Synthesis and Electrochemical Characteristic of Si/C Composite Anode with CNF for Lithium Ion Battery

s2b-008

Philippe Mandin *(Electrochemical Engineering, South Brittany University, Lorient, France)*, Envel Guezennec, Yann Le Guennec, Pascal Morançais, Alexandre Solacolu

Hydrogen production from water electrolysis for the storage of offshore wind energy

s2b-009

Kwang Chul Roh *(Energy & Environmental Division, Korea Institute of Ceramic Engineering & Technology, Seoul, Korea)*, Joong Tark Han, Mok-Hwa Kim, Kwang-Bum Kim, Ho Seok Park, Sol Yun

Retransformed graphitic activated carbon from ionic liquid-derived carbon containing nitrogen

s2b-010

Taeseup Song *(Hanyang University, Seoul, Korea)*, Yeon-Gil Jung, Ungyu Paik, Hyunjung Park, Jihoon Seo

Three-dimensional Hierarchical TiO_2 Nanotubes - Carbon Nanofiber Nanostructure as an Anode for High Energy and Power Lithium Ion Batteries

s2b-011

Yoshiharu Uchimoto *(Graduate School of Human and Environmental Studies, Kyoto University, Kyoto, Japan)*

In operando synchrotron X-ray analysis of lithium ion cathode reaction

s2b-012

Ken-Ming Yin *(Department of Chemical Engineering, Yuan Ze University, Chung Li, Taiwan)*, Bo-Syun Cheng, Hsiao-Kuo Hsuen, Yu-An Kung

A Discussion on the Water Treatment of Two-phase Flow in the Membrane Electrode Assembly of PEMFCs

s2b-013

Marketa Zukalova *(Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic)*

Differences in Li-storage Mechanism into Anatase and TiO_2(B)

Session 2

Symposium 2c: Applications; Electrochemistry in biological systems

s2c-001

Thi Mai Thanh Dinh *(Corrosion and Protection of Metals, Institute for Tropical Technology, Hanoi, Viet Nam)*

Impact of parameters on electrodeposition of nanocrystalline apatite coating on 316L stainless steel

s2c-002

Akbar Islamnezhad *(Chemistry Department, Islamic Azad University, Rasht, Iran)* Hassan Kefayati, Maryam Valizadeh

Cyclic Voltammetric Investigation of Electrosynthesized Pyrano[2,3-d]Pyrimidinones s2c-003

Xianchan Li *(Department of Chemistry of Molecular Biology, University of Gothenburg, Gothenburg, Sweden)*, Andrew G. Ewing, Soodabeh Majdi

Amperometric Quantitative Measurements of Individual Vesicular Contents in Single Cells

s2c-004

Katerina Novakova *(Institute of Environmental and Chemical Engineering, University of Pardubice, Pardubice, Czech Republic)*, Jaromira Chylkova, Jana Jaklova Dytrtova, Jan Langmaier, Tomas Navratil, Ivana Sestakova, Romana Sokolova

Elucidation of Transport of Environmentally Important Compounds across Model Membranes

s2c-005

Piotr Pieta *(Department of Physical Chemistry of Supramolecular Complex, Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland)*, Michael Grossutti, Jacek Lipkowski, ZhangFei Su

Electrochemical, PMIRRAS, and ATR-IR Characterization of a New Bacteriocin-like Antimicrobial Peptide at a Model Biological Membrane

s2c-006

Libuse Trnkova *(Department of Chemistry, Masaryk University, Faculty of Science, Brno, Czech Republic)*, Ondrej Laskafeld, Premysl Lubal, Iveta Pilarova

The Oxidation Processes of Benzylaminopurines at Pencil Graphite Electrodes Modified by Monovalent Copper Ions

s2c-007

Lin Zhang *(LCPME, CNRS and Université de Lorraine, Villers-lès-Nancy, France)*, Mathieu Etienne, Gert-Wieland Kohring, Ievgen Mazurenko, Neus Vilà, Alain Walcarius

Immobilization of dehydrogenases on macroporous carbon felt by click chemistry for electroenzymatic synthesis

Symposium 2d: Applications; Electrochemical sensors and biosensors

s2d-001

Cesar Alfredo Barbero *(Chemistry, National University of Rio Cuarto, Rio Cuarto, Argentina)*, Diego Acevedo, Rusbel Coneo Rodriguez, Gabriel Planes

Strong Catalytic Effect of Cobalt Oxide Nanoparticles on the Electrochemical Sensing of Arsenic

s2d-002

David Bower *(Chemistry, La Trobe University, Bundoora, Australia)*, Conor Hogan

Co-reactant Electrogenerated Chemiluminescece (ECL) from Carbon Dioxide in Ionic Liquids

s2d-003

Cecilia Cristea *(Department of Analytical Chemistry, University of Medicine and Pharmacy Cluj-Napoca, Cluj-Napoca, Romania)*, Anca Florea, Iuliu Ovidiu Marian, Robert Sandulescu, Mihaela Tertis

Electrochemical Studies on Carbon Based Electrodes Modified with Single and Multi -wall Carbon Nanotubes - Polymer Nanocomposites

s2d-004

Laura Fernández Llano *(R&D, DropSens, S.L., Llanera, Spain)*, Pablo Fanjul-Bolado, M. Begoña González-García, David Hernandez-Santos

Thin layer disposable flow cells as electrochemical detectors in FIA system

s2d-005

Ezat Hamidi-Asl *(Department of Chemistry, University of Antwerp, Antwerp, Belgium)*, Ronny Blust, Freddy Dardenne, Karolien De Wael

Effect of Nanoparticles on the Efficiency of Aptasensors: A Comparative Study and the Aptamer of *E. coli* as a Model

s2d-006

Zofia Iskierko (*Department of Physical Chemistry of Supramolecular Complexes, Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland)*, Anna Checinska, Krzysztof Fronc, Wlodzimierz Kutner, Krzysztof Noworyta, Piyush Sindhu Sharma

Extended-gate field-effect transistor (EG-FET) as the transducer in a chemosensor for stereoselective D- and L-phenylalanine determination s2d-007

Akbar Islamnezhad *(Chemistry Department, Islamic Azad University, Rasht, Iran)*, Nasibeh Kouchaknezhad

Voltammetric Rizatriptan Nanobiosensor

s2d-008

Carlos Pereira *(Chemistry and Biochemistry, University of Porto, Porto, Portugal),* Inês Miranda, Fernando Silva, Laura Sousa

Electropolymerized Molecularly Imprinted Electrodes for Amylase Sensing

s2d-009

Abbas Shirmardi *(Chemistry, Islamic Azad University Masjed-Soleyman Branch, Masjed-Soleyman, Iran)*, Morteza Akhond, Mojtaba Shamsipur

Electronic Tongue for Simultaneous Determination of Cyanide, Thiocyanate and Iodide

s2d-010

Vlastimil Vyskoèil *(Department of Analytical Chemistry, Faculty of Science, Charles University in Prague, Prague, Czech Republic)*, Marta Blašková, Andrea Hájková, Christian Iffelsberger, Zuzana Jureèková, Frank-Michael Matysik,

Complex Electrochemical Detection of Damage to DNA Using Simple Label-free DNA Biosensors

Symposium 2e: Applications; Nanostructured materials

s2e-001

Ya Yun Chan *(Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore, Singapore)*, Alex Eng, Martin Pumera, Richard Webster

Does Modifying Electrodes via the Drop Casting Method Provide a Complete Coverage over the Underlying Electrode Surface?

s2e-002

Damaris Fernandez *(School of Chemistry & CRANN/AMBER, Trinity College Dublin, Dublin, Ireland)*, Michael E.G. Lyons, Luis Romeral

Magneto-electrochemical interactions during phase transitions at nano/micro structured macro-electrodes s2e-003

Jose Garcia Anton *(Ingeniería Quimica y Nuclear, Universidad Politecnica de Valencia, Valencia, Spain)*, Ramon Manuel Fernandez-Domene, Dionisio García-García, Maria Teresa Montañes, Rita Sánchez-Tovar

New Morphologies of Nanostructures Obtained by Zn Anodization under Flowing Conditions

s2e-004

Jose Garcia Anton *(Ingeniería Quimica y Nuclear, Universidad Politecnica de Valencia, Valencia, Spain)*, Ramon Manuel Fernandez-Domene, Dionisio García-García, Maria Jose Muñoz Portero, Rita Sánchez-Tovar

WO_3 Photoanodes for Hydrogen Production

s2e-005

Corinne Lagrost *(Institut des Sciences Chimiques de Rennes, CNRS and Université de Rennes 1, Rennes, France)*, Xiaoyan He, Stéphane Rigaut, Yves-Marie Hervault, Andrea Mulas, Lucie Norel

Fast redox communication at acetylides – ruthenium thiols, dithiocarboxylic acid and isocyanide SAMs on gold

s2e-006

Yann Leroux *(Institut des Sciences Chimiques de Rennes, CNRS, Université de Rennes 1, Rennes Cedex, France)*, Philippe Hapiot

Nanostructured Monolayers on Carbon Substrates

s2e-007

Robert Sandulescu *(Analytical Chemistry Dept., Iuliu Hatieganu University of Medicine and Pharmacy, Cluj-Napoca, Romania)*, Cecilia Cristea, Luminita Fritea, Oana Hosu, Mihaela Tertis

Characterization of Innovative Graphene-based Modified Electrodes for Pharmaceutical Analysis

s2e-008

Monica Santamaria *(DICAM, Università di Palermo, Palermo, Italy)*, Giorgio Conigliaro, Francesco Di Franco, Francesco Di Quarto, Roberto Macaluso, Shahab Miraghaei, Mauro Mosca

Multiscale Approach in Studying the Influence of Annealing Conditions on Conductivity of TiO_2 Nanotubes s2e-009

Maria Elena Vela *(Laboratory of Nanoscopies and Surface Physical Chemistry, INIFTA (Conicet-UNLP), La Plata, Argentina)*, B. Auguié, F. Castez, E. Cortes, M.A. Daza Millone, A. Fainstein, L.A. Guerra, R.C. Salvarezza

Role of surface roughness in the SERS response of Au-nanocavities

Symposium 2f: Applications; Corrosion and protection

s2f-001

Laidi Babouri *(Chemistry, Ecole Normale Supérieure d'Enseignement Technologique, Skikda, Algeria)*, Abdessalem Abdelouas, Kamel Belmokre, Yassine El Mendili, Abdenour Kabir

Study of the stability of the passive film formed on copper-based binary alloys in 3% NaCl solution

s2f-002

Sofia Benamirouche *(Laboratory of Electrochemistry and Corrosion, Military School Polytechnic, Algiers, Algeria)*

Relationship between the precipitation and electrochemical behavior of aluminum alloy type 2017A

s2f-003

Silviu Iulian Drob *(Electrochemistry and Corrosion, Institute of Physical Chemistry, Bucharest, Romania)*, Thierry Gloriant, Doina Margareta Gordin, Cora Vasilescu

Synthesis, mechanical characterization, electrochemical and corrosion behaviour of titanium-based alloy with "super" properties

s2f-004

Paula Fernandes *(Chemistry and Biochemistry, University of Porto, Porto, Portugal)*, Carlos Pereira, Fernando Silva

Electrodeposition of nickel using eutectic mixtures based in ionic liquid formulations s2f-005

Noureddine Madaoui *(Division des Milieux Ionises et Lasers, Centre de Développement des Technologies Avancées, Alger, Algeria)*, Samia Belhousse, Abdelkader Hammouche, Kamilia Kheyar, Sawsen Nezar, Nadia Saoula, Chaffia Yaddaden

Protection of stainless steel for corrosion application by titanium dioxide PVD coating in 3.5% NaCl solution

s2f-006

Anh Son Nguyen *(Institut Carnot CIRIMAT, ENSIACET, Toulouse, France)*

Local electrochemical impedance spectroscopy applied to the corrosion protection of waterborne coatings on a 2024 aluminium alloy

s2f-007

Ricardo M. Souto *(Department of Chemistry, University of La Laguna, La Laguna (Tenerife), Spain)*, Bibiana M. Fernández-Pérez, Javier Izquierdo, Juan J. Santana

Imaging of Concentration Distributions on Corroding Magnesium Exposed to Aqueous Environments using Scanning Electrochemical Microscopy

s2f-008

Cora Vasilescu *(Electrochemisty and Corrosion, Institute of Physical Chemistry, Bucharest, Romania)*, Jose Maria Calderon Moreno, Silviu Iulian Drob, Petre Osiceanu

Corrosion resistance of new ternary Ti-Ta-Zr alloy in artificial saliva simulating severe functional conditions

s2f-009

Maria Elena Vela *(Laboratory of Nanoscopies and Surface Physical Chemistry, INIFTA (Conicet-UNLP), La Plata, Argentina)*, G. Benitez, L. Gassa, E.D. Prieto, M.P. Quiroga Argañaraz, J. Ramallo-López, A. Rubert, R.C. Salvarezza

Improvement of the corrosion resistance of Ni-W coatings on steel using a mixed silane film

Index

DROPSENS

Innovative Technology for Miniaturised Electrochemistry

SPELEC

SPECTROELECTROCHEMISTRY IN ONE BOX

· ONE INSTRUMENT
· ONE SOFTWARE

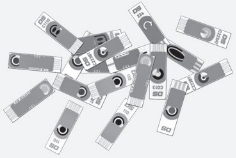
PORTABLE POTENTIOSTATS/GALVANOSTATS

STAT8000

STAT400

DROPSTAT

SCREEN-PRINTED ELECTRODES



www.dropsens.com
info@dropsens.com

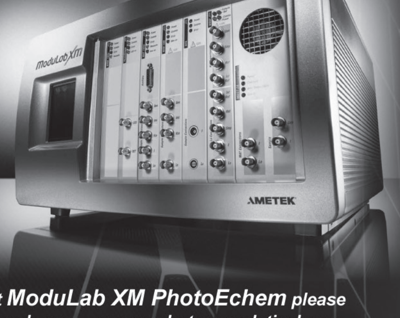
Princeton Applied Research

solartron analytical

ModuLab® XM PhotoEchem

Comprehensive Photovoltaic Techniques:

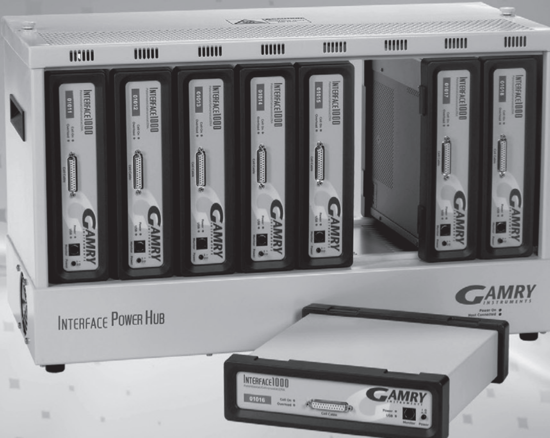
IPCE, EIS, IMPS, IMVS
Photovoltage Decay
Charge Extraction



AMETEK®

For more information about **ModuLab XM PhotoEchem** please
www.princetonappliedresearch.com www.solartronanalytical.com
pari.info@ametek.com Solartron.info@ametek.com

The Most Flexible
Multichannel Potentiostat



Keep everything in a single chassis or undock your channels and move them closer to your cell. Closer to cell = Shorter cell cables = Better results.

- Up to 5 A per Channel
- EIS to 1 MHz at >99% Accuracy on Every Channel
- Fully Isolated from Earth Ground
- Independent, Simultaneous Measurements
- Undock Individual Channels for Flexible Placement

Now with the NEW
INTERFACE5000

GAMRY
INSTRUMENTS
www.gamry.com

Discover Autolab RRDE

The new Autolab RRDE

The Autolab Rotating Ring Disc Electrode (RRDE) is the latest addition to the Metrohm Autolab accessories for electrochemical measurements.
The Autolab RRDE can be used to perform electrochemical measurements under controlled hydrodynamic conditions.

The Autolab RRDE uses 2 identical friction-less mercury contacts for ultra-low noise measurements and can be used with any Autolab potentiostat/galvanostat fitted with the BA, dual-mode bipotentiostat module.

The Autolab RRDE is provided with a motor controller that can be operated manually or by the NOVA software. The rotation rate can be specified between 100 RPM and 10,000 RPM in 1 RPM steps.

The Autolab RRDE electrode tips are fitted with a 5 mm electrode disc and a thin concentric platinum ring.
The electrode disc is availalble in Gold, Platinum or Glassy Carbon. The RRDE electrode tips are dimensioned with an electrode gap of 375 µm and a theoretical collection efficiency of 24.9 %.

SPECIFICATIONS	Autolab RRDE
• Speed control	Manual or by NOVA software
• Motor speed range	100 - 10,000 RPM +/- 1 RPM
• Acceleration/deceleration	4,000 RPM/s
• Maximum disc current	500 mA
• Maximum ring current	50 mA
• Contact	Double sealed Hg pool
• Electrode tips	Pt disc/Pt ring, Au disc/Pt ring, GC disc/Pt ring
• Collection efficiency	24.9 %
• Electrode gap	375 µm

3 year
instrument warranty

Dedicated to research

www.metrohm-autolab.com

Metrohm
Autolab B.V.

Electrochemical Studies of Nanoparticles

Richard G Compton
Oxford University, United Kingdom
Department of Chemistry, Physical and Theoretical Chemistry Laboratory
South Parks Road, Oxford, OX1 3QZ
Richard.compton@chem.ox.ac.uk

Recent progress in the electrochemical study of single nanoparticles by means of the nano-impacts approach will be surveyed and evaluated

The design of electrodes and nano-impacts methodology allowing the electrochemical sizing of nanoparticles as small as 4nm will be described, and shown to be applicable to nanoparticle concentrations as low as 0.1 pM.

Contrasts will be drawn between experiments conducted on ensembles of nanoparticle, as in nanoparticle modified electrodes, and the behavior contrasted seen for single nanoparticle experiments. Important factors include the change of mass transport regime, altered apparent electrochemical reversibility and the incomplete ‘stripping’ seen for aggregated nanoparticles.

The role of surface charge on the observed electrochemical behavior will be explored with reference to experiments carried out using indigo nanoparticles in weakly supported aqueous electrolytes.

Experiments with diverse types of nanoparticles will be reported, namely metallic (Ag, Cu, Ni, Au), metal oxides (Fe_30_4), organic (indigo and oil blue) and polymeric (poly-N-vinyl carbazole) as well as studies on single drug encapsulating liposomes

Finally a speculative electrochemical perspective on the origins of the toxicity of silver nanoparticles will be offered.

References

“The electrochemical detection and characterization of silver nanoparticles”, Y Zhou, N V Rees and R G Compton, Angewandte Chemie International Edition, 50, 2011, 4219

“Electrochemical sizing of organic nanoparticles”, W Cheng, X Zhou and R G Compton, Angewandte Chemie International Edition, 52, 2013, 12980

“Electrochemical observation of single collision events: fullerene nanoparticles”, E J E Stuart, K Tschulik, C Batchelor-McAuley and R G Compton, ACS Nano, 8, 2014, 7648

“Organic nanoparticles: mechanism of electron transfer to indigo nanoparticles”, W Cheng, C Batchelor-McAuley and R G Compton, ChemElectroChem, 1, 2014, 714

“Doping of single polymeric nanoparticles”, X Zhou, W Cheng and R G Compton, Angewandte Chemie International Edition, 53, 2014, 12587

“Investigation of single drug encapsulating liposomes using the nano-impact method, W Cheng and R G Compton, , Angewandte Chemie International Edition, 53, 2014, 13928

“Why are silver nanoparticles more toxic than bulk silver? Towards understanding the dissolution and toxicity of silver nanoparticles”, C Batchelor-McAuley, K Tschulik, C C M Neumann, E Laborda and R G Compton, International Journal of Electrochemical Science, 9, 2014, 1132

In-Situ Surface Enhanced Raman Spectroscopic Studies On Electrochemical Interfaces: From Molecular Intermediates to Surface Morphology

Zhong-Qun Tian
State Key Laboratory of Physical Chemistry of Solid Surfaces, and Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University
*Xiamen, China*s
e-mail: zqtian@xmu.edu.cn

Surface enhanced Raman scattering has been used to study electrode/electrolyte interface since its discovery, as an important member of a few in-situ methods. As a molecular spectroscopy, SERS is good at revealing the molecular structure. The giant enhancement on the Raman intensity allows detecting the surface species in electrochemical interface whose coverage is even lower than one monolayer, such as precursor or reaction intermediate. Thus, SERS is a powerful tool for the investigation of electrochemical kinetics. Recently, we employed SERS to study the mechanism of the catalytic electrochemical reduction of benzyl chloride on Ag. With the support of DFT calculation and Raman scattering theory, we found a weakly adsorbed benzyl chloride precursor and strongly adsorbed benzyl radical/anion intermediates. The identification of the surface species during potential movement finally supported a comprehensive consideration on the mechanism regarding elementary steps and reaction energy.

Meanwhile, SERS is regarding with the local surface morphology, not only in term of surface plasmon but also the adsorption configuration, which is promising to reveal the surface morphology. CO has been found to be sensitive to the molecular coverage. We discovered a highly catalytic Au-core Pd-shell Pt-cluster trimetallic nanoparticle (Au@Pd@Pt NPs) for electro-oxidation of formic acid. However, the source of catalytic activity is ambiguous. We employed electrochemical SERS to study the adsorption of CO. Based on fitting the experimental spectra with DFT calculation, a unique mushroom-like structure is unearthed and a new NP growth mode is proposed. Such mushroom-like structure provides more novel active sites with more coordinate number favorably for specific reactions.

In the highlight of these works, it can be found in-situ electrochemical SERS could be a powerful tool for a multi scale study on electrochemical interface beyond the molecular spectroscopy. I will provide the details in the lecture.

Reference:

1. Wang, A.; Huang, Y. F.; Sur, U. K.; Wu, D. Y.; Ren, B.; Rondinini, S.; Amatore, C.; Tian, Z. Q. J. Am. Chem. Soc. 2010, 132, 9534.
2. Huang, Y. F.; Wu, D. Y.; Wang, A.; Ren, B.; Rondinini, S.; Tian, Z. Q.; Amatore, C. J. Am. Chem. Soc. 2010, 132, 17199.
3. Duan, S.; Fang, P.-P.; Fan, F.-R.; Broadwell, I.; Yang, F.-Z.; Wu, D.-Y.; Ren, B.; Amatore, C.; Luo, Y.; Xu, X.; Tian, Z.-Q., Phys. Chem. Chem. Phys. 2011, 13, 5441-5449
4. Fang, P.-P.; Duan, S.; Lin, X.-D.; Anema, J. R.; Li, J.-F.; Buriez, O.; Ding, Y.; Fan, F.-R.; Wu, D.-Y.; Ren, B.; Wang, Z. L.; Amatore, C.; Tian, Z.-Q., Chemical Science 2011, 2, , 531-539.

A Scanning Probe Investigation of Inter-Granular Corrosion in Sensitized Stainless Steel Nuclear Fuel Cladding

Ronald Clark, Steve Walters*, Geraint Williams
Materials Research Centre, College of Engineering, Swansea University, Singleton Park, Swansea, SA2 8PP, UK.
**National Nuclear Laboratory, Harwell Science Campus, Didcot, Oxfordshire, OX11 0QT, UK*
798741@swansea.ac.uk

Spent nuclear fuel from advanced gas-cooled nuclear reactors, housed inside tubes of an austenitic, niobium-stabilized stainless steel is subjected to long term pond storage, pending final geological disposal. The cladding alloy comprising 20% Chromium (Cr) and 25% Nickel (Ni) is susceptible to radiation induced sensitization (RIS) caused by protracted exposure to a combination of high neutron flux and elevated temperature within the reactor core. This leads to the redistribution of alloying elements at a microstructural level, the neutron bombardment causing vacancies which diffuse towards grain boundaries and counter-diffusion of Cr atoms, thus causing depletion of Cr in regions adjacent to these boundaries. The sensitized cladding alloy therefore becomes susceptible to inter-granular corrosion (IGC), especially in chloride containing aqueous solution. This effect may be simulated by thermal processing, forming chromium carbide precipitates at grain boundaries, another means of reducing the local concentration of Cr atoms available in the alloy. This paper focuses on characterizing localized corrosion behavior in cladding alloy both in the as-received and thermally sensitized state. A combination of conventional d.c. potentiodynamic studies and *in-situ* scanning vibrating electrode mapping is used to establish the dependence of localized corrosion initiation and propagation on chloride ion concentration, temperature and pH in aqueous solution. When polarized to potentials greater than its breakdown potential (E_b), the localized corrosion of Nb-stabilized cladding in an unsensitized condition takes the form of pitting rather than IGC. In deaerated aqueous sodium chloride (NaCl), at near-neutral pH, the unsensitized alloy exhibits a dependence of E_b on chloride concentration ($[Cl^-]$) such that $E_b = A + B \log_{10}[Cl^-]$, where A = 0.41 V (vs SCE) and B = -0.09 V/decade. However, for thermally sensitized alloy specimens, anodic polarization in high concentration NaCl electrolyte produces significant IGC, while the same experiments carried out in more dilute electrolyte tends to favour the propagation of discrete pits. These observations are confirmed by scanning electron microscopy of electro-etched, post-corrosion sensitized alloy specimens. A scanning vibrating electrode technique (SVET) used in combination with anodically polarized alloy specimens is employed *in-situ* to study the initiation and propagation of IGC in concentrated NaCl electrolyte. Changes in local current density values measured over regions of local anodic activity are used to follow the kinetics of IGC propagation and the periodic initiation of new local anodes areas subsequent to initial breakdown. In-situ SVET investigations are complemented by the use of optical time-lapse microscopy of etched cladding alloy surfaces in order to correlate IGC initiation locations with microstructural features. Figure 1 shows typical results obtained for a sensitized stainless steel surface immersed in 1 mol dm^{-3} NaCl (aq) contained in a bespoke flow cell, which allows specimens to be anodically polarised *in-situ*. Figure 1 clearly shows localised corrosion initiating at a grain boundary location (a) and subsequently propagating simultaneously along several neighbouring boundaries (b and c). Finally scanning Kelvin probe microscopy (SKPFM) is used to identify the relative nobility of inclusions and grain boundaries, with particular emphasis on regions of the grains adjacent to grain boundaries in the sensitized alloy.

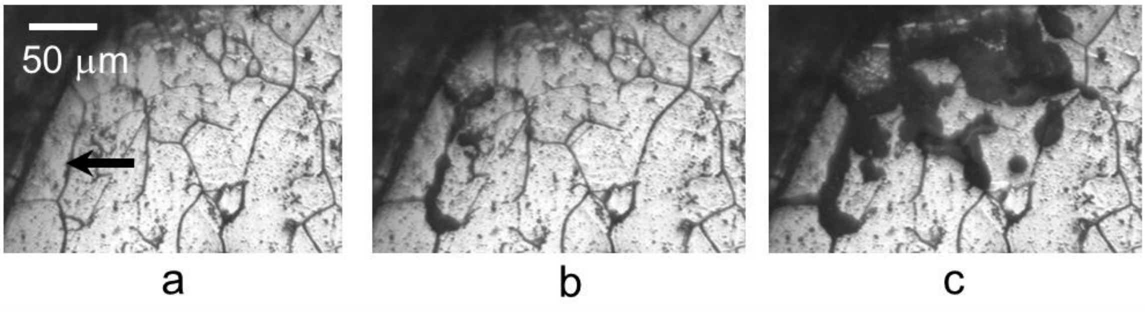


Figure 1: Optical micrographs of an anodically polarised AISI 310 stainless steel surface in 1M NaCl (aq), showing (a) initiation, (b) propagation and (c) final extent of IGA attack. The arrow in (a) indicates the IGA initiation point.

Sharp-interface model of electrodeposition and dendritic growth

Christoffer P. Nielsen, Henrik Bruus
Department of Physics, Technical University of Denmark
DTU Physics Building 309, DK-2800 Kongens Lyngby, Denmark
chnie@fysik.dtu.dk

Electrodeposition from an electrolyte onto a metal electrode is an important step in a range of systems and processes, e.g. for batteries, electroplating, and synthesis of semiconductor thin films, nanostructures, and powders [1]. Despite a wealth of interest in the problem, it has proven difficult to quantitatively model the electrodeposition process. Those difficulties are both due to the nonlinear transport and reaction processes in the system [2] and, in particular, due to the tendency of the electrode surface to go unstable and form dendritic structures with a large range of length scales.

The electrodeposition models that do exist have opted to use phase-field methods, similar to those that have been quite successful in modelling solidification processes [3]. While the phase-field models do predict some kind of dendritic growth at the electrode surface, it seems to us that they have some fundamental shortcomings when applied to an electrochemical system: Firstly, a phase-field model cannot properly implement the nonlinear Butler-Volmer reaction rate at the electrode. Secondly, it has been known since 1990 [4] that the extended space-charge region, forming at overlimiting currents, greatly affects the electrodeposition process. Nevertheless, the phase-field models assume local electroneutrality in the electrolyte.

To address these issues, we have developed a sharp-interface model of electrodeposition, which includes the Butler-Volmer surface reaction and allows for a net charge density in the electrolyte. This sharp-interface model is an extension of our recent bulk electrokinetics model [5]. To validate the model we have extended the stability analysis of Sundstrom and Bark [6] to the case of overlimiting currents and non-zero space charge densities. We have yet to make a thorough comparison between model predictions and published experimental results, but a preliminary survey does indicate that our model correctly predicts the transitions between different growth regimes as the current is varied.

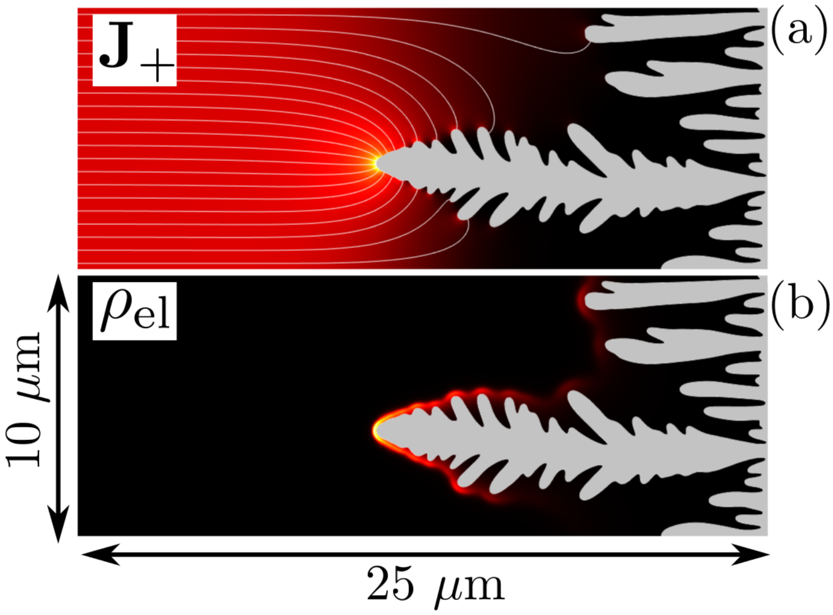


Figure 1. Dendritic electrode (gray) after deposition for 25 minutes with a bias voltage of 20 k_BT/e. (a) Magnitude of the current density J_+ (color plot) and its streamlines (white lines). (b) Magnitude of the space charge density ρ_{el} (color plot).

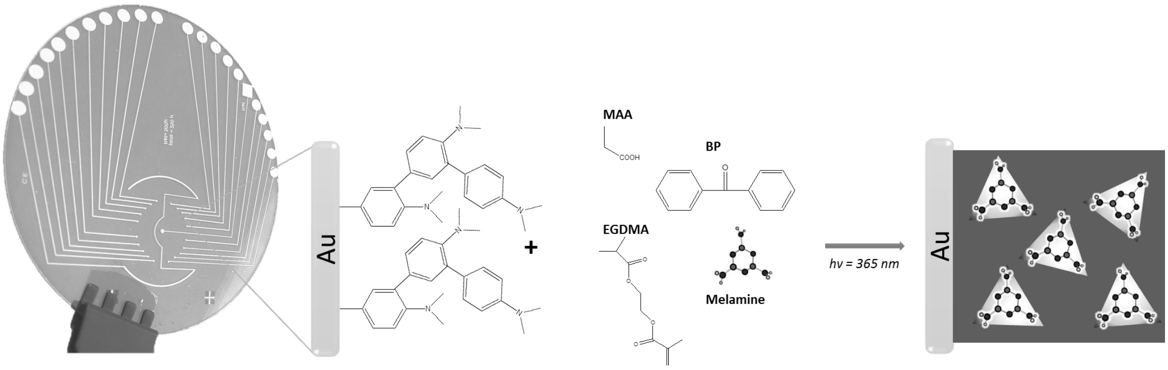
1. M. Rosso, Electrochim. Acta **53** (2007) 250-256
2. M. Bazant, Accounts Chem. Res. **46** (2013) 1144-1160
3. Y. Shibuta, Y. Okajima, T. Suzuki, Sci. Technol. Adv. Mat. **8** (2007) 511-518
4. J. N. Chazalviel, Phys. Rev. A **42** (1990) 7356-7367
5. C. P. Nielsen, H. Bruus, Phys. Rev. E **90** (2014) 043020
6. L. G. Sundström, F. H. Bark, Electrochim. Acta **40** (1995) 599-614

Design of Portable Sensor to Detect Hazardous Molecules in our Environment.

I. Mazerie [a], I. Bakas [b], M.M. Chehimi [c], B. Carbonnier [c], A. Girard [d], P. Didier [e], F. Razan[e], N. Coulon [f], D. Floner [a], F. Geneste [a],
a) ISCR UMR-CNRS 6226, University of Rennes 1, Campus de Beaulieu, 35042 Rennes, b) ITODYS UMR-CNRS 7086, University of Paris Diderot, Rue Jean Antoine de Baïf, 75205 Paris, c) ICMPE UMR 7182, University of Paris-Est, rue H. Dunant F, 94320 Thiais, d) IMN UMR6502, Campus Sciences, rue de la Houssinière, 44322 Nantes, e) SATIE UMR CNRS 8029, ENS Rennes, Campus de Ker Lann, 35170 Bruz, f) IETR, University of Rennes 1, Campus de Beaulieu, 35042 Rennes.
Isabelle.Mazerie@univ-rennes1.fr

As in many domains, safety rests partly on the development of reliable high sensitivity analytical methods to target hazardous molecules. Therefore there is a need for developing simple methods for diagnosis of the target beneficial or harmful molecules in food products or in our environment. It is well known that performance of solid electrodes may be drastically altered by various processes such as adsorption of organic or inorganic species on the electrode, leading sometimes to the passivation of the electrode surface. This kind of irreversible process can be circumvented by using dropping mercury electrode with continually fresh Hg surface and new drop every few seconds. However, due to the toxicity of Hg and of technical inconveniences, colorimetric or spectrophotometric techniques are the most frequently used methods for long-term on-line analysis or for field measurements, despite the fact that they are less sensitive than electroanalysis.

Our team has developed a new concept of device based on sampled-current voltammetry performed on an electrode array.[1,2] In fact a single electrochemical measurement is performed independently and differently on each electrode in the array. Each electrode plays a similar role than a dropping Hg electrode in polarography and the renewal of the electrode surface and of the solution in the proximity of the electrode is assured. However, the sensitivity of the method is strongly dependent of the affinity between the surface and the analyte and the selectivity is only obtained by the oxidation or reduction potential of the analyte. Consequently, the use of modified surfaces allowing the selective preconcentration of the analyte on the electrode array should improve the performances of the sensor.
An example of application of this original method with molecular imprinted polymer (MIP) will be presented for melamine detection, a molecule artificially added in milk which is harmful or even fatal to the human kind. The MIP was prepared by electrografting of the photoinitiator on the electrode surface followed by photopolymerization.[3] The electrochemical response performed on the electrode array was enhanced compared with classical linear voltammetry.



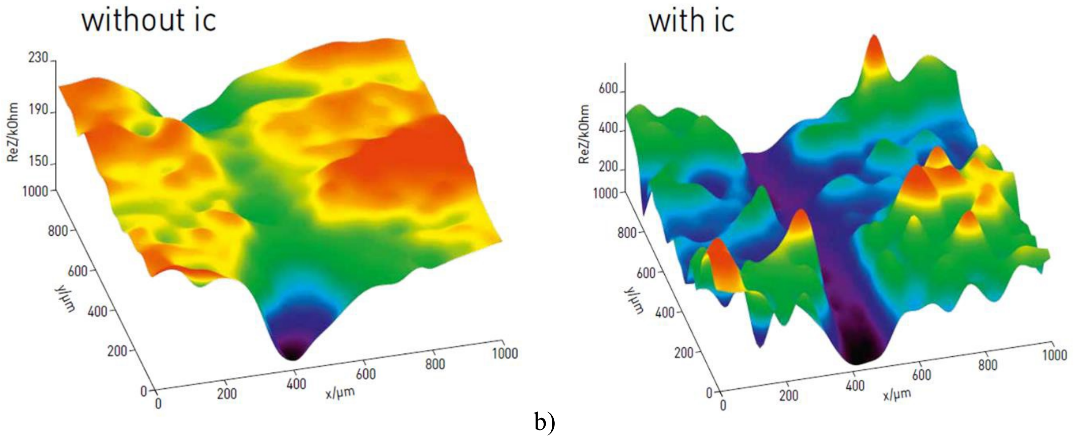
Schematic illustration of the sensor design for Melamine detection

1. L. Mignard, M. Denoual, O. Lavastre, D. Floner, F. Geneste, *J. Electroanal. Chem.*, ***689***, 83-87 (2013).
2. O. Lavastre, D. Floner, F. Geneste, PCT Int. Appl. **WO 2006108759**, (2006).
3. M.M. Chehimi, S. Gam-Derouich, A. Madani, PCT Int. Appl. **WO 2012028825**, (2011).
4. I. Bakas, Z. Salmi, M. Jouini, F. Geneste I. Mazerie, D. Floner, B. Carbonnier, Y. Yagci, M.M. Chehimi, *Electroanalysis*, **27**, 1-12 (2015).

Using intermittent contact (ic) SECM for corrosion and energy storage materials investigation.

Nicolas Murer, *Bio-Logic SAS*
1 Rue de l'Europe, 38640 Claix, France
nicolas.murer@bio-logic.net
Samantha Catarelli, Daniel Lonsdale, John Griffiths
Uniscan instruments Ltd.
Pinewood Court, Larkwood Way, Tytherington Business Park,
Macclesfield, Cheshire, SK10 2XR.United Kingdom.

ic-SECM is an operation mode of SECM that was first developed by the University of Warwick[1,2]. In this mode of operation, the topography of the sample during an SECM or ac-SECM measurement can be tracked, hence removing any contribution of the topography to the electrochemical response measured at the probe tip. This means that highly non-planar or rough sample can be studied, and the response measured at the probe will only contain electrochemical information. Furthermore, the response dynamics will be maximized. In this presentation, we will show a few examples of results in two applications: corrosion and energy storage. In both applications, the various benefits of using SECM and/or ac-SECM in ic mode will be demonstrated as well as the unique type of information that can be obtained using SECM. New knowledge about energy storage electrode materials and corrosion mechanisms in metals become available.



a) b)

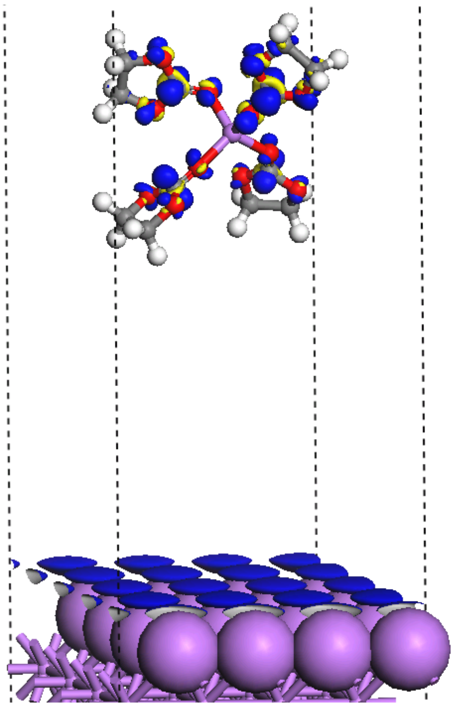
ac-SECM picture of an 7075 scratched sample in 0.1 mol/L KCl a) without intermittent contact, b) with intermittent contact.

1. K. Mc Kelvey, M. A. Edwards, P. R. Unwin, Anal. Chem. 2010, 82, 6334–6337
2. K. Mc Kelvey, M. E. Snowden, M. Perulo, P. R. Unwin, Anal. Chem. 2011, 83, 6447–6454

Ab Initio Modeling of Solvent-Metal Electrochemical Interface

Jean-Sébastien Filhol, Nicolas Lespès
Institut Charles Gerhardt, Université Montpellier2
Montpellier France
filhol@univ-montp2.fr

The electrochemical interface is fundamental to understand electrochemical reactions either for electrocatalysis applications (fuel cells), corrosion, electroplating or for electrochemical energy storages such as Li-ion batteries. Nevertheless, it is extremely complex to model not only because of the occurring electrochemical effects but also because of the complexity of the electrode-solvent interface. Classical models fairly well reproduce the behavior of such an interface by introducing more or less complex description of the electric double layer (Helmholtz plane, diffuse layer etc.), but are oblivious to the quantum phenomena occurring at the interface. Ab initio approaches can describe this quantum behavior with good accuracy, nevertheless most of these approaches are not accounting the full complexity of the electrochemical interface as it would necessitate including the solvent (at least hundreds/thousands of molecules) and electrolyte (with their interaction with the solvent and the surface) in their structural and time-dependent dimension leading to too costly calculations. We will present an implicit solvent approach (exemplified by a Li/Ethylene carbonate (EC) interface) that allows recovering the proper electrochemical properties such as surface capacitance at a limited cost. We will highlight the effect of the model parameters on the quality of the calculation. We will in particular discuss how implicit/explicit model should be used in order to recover the potential stability for Li-electrodes in carbonate solvents and how the electrode growth or consumption is linked with the local chemical/electrochemical parameters. Finally, we will show using the Fukui function tool previously developed that the redox species involved in the reduction of Li^+ should include the first solvation sphere.



Fukui function for a Li+(EC)^4/Li interface.

Computational Electrocatalysis: Novel Materials For Oxygen Reduction Reaction (ORR) And Methanol Oxidation Reaction (MOR)

Cristiana Di Valentin
Dipartimento di Scienza dei Materiali, Università di Milano Bicocca
via R. Cozzi 55 20125 Milano Italy
cristiana.divalentin@mater.unimib.it

Novel materials are continuously proposed to substitute platinum at fuel cells electrodes. Here we investigate, by means of computational electrochemistry, based on density functional theory (DFT) calculations, two promising C-based alternatives for an efficient catalysis of the oxygen reduction reaction (ORR) at the cathode and the alcohol oxidation reaction (AOR) at the anode: non-metal doped graphene and tungsten carbide, respectively.

ORR: Among non-metal doped graphenic systems, B-doped graphene has been reported to be the most efficient for the ORR [1]. Here, we first present the oxygen reactivity on the B-doped graphene surface in terms of intermediates and transition structures along the various possible reaction pathways [2,3]. Then, we analyze the free energy diagrams along the four-reduction steps with the methodology by Nørskov and co. [4] in both acidic and alkaline conditions and describe the pH effect on the stability of the intermediates of reduction in terms of the Pourbaix diagram. Finally, we briefly present a recent comparative computational/experimental study of B-doped and B,N-codoped graphene QD systems [5].

AOR: Polycrystalline tungsten carbide films have been reported to catalyze alcohols oxidation reaction [6,7]. Here, we determine the reaction mechanism, the free energy profiles and estimate the expected overpotential for the full oxidation process of methanol to water and carbon dioxide as electrochemically catalyzed by the two most stable basal and prismatic WC surfaces, (0001) and (10-10), in comparison with the traditional Pt (111) surface [8]. We find that the basal plane is more efficient and performs at overpotentials which are competitive to those of Pt. The preferred path is the direct one, which does not involve the CO intermediate formation.

[1] Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Quiao JACS 136 (2014) 4394
[2] L. Ferrighi, M. Datteo, C. Di Valentin JPC C 118 (2014) 223
[3] G. Fazio, L. Ferrighi, C. Di Valentin J. Catalysis 318 (2014) 203
[4] J. K. Nørskov, J. Rossmeils, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Blgaard, H. Jonsson JPC B 108 (2004) 17886
[5] M. Favaro, L. Ferrighi, G. Fazio, L. Colazzo, C. Di Valentin, C. Durante, F. Sedona, A. Gennaro, S. Agnoli, G. Granozzi ACS Catal. 5 (2015) 129
[6] E. C. Weigert, A. L. Stottlemyer, M. B. Zellner, J. G. Chen JPC C 111 (2007) 14617
[7] Z. J. Mellinger, T. G. Kelly, J. G. Chen ACS Catal. 2 (2012) 751
[8] C. Di Valentin, D. Fittipaldi, G. Pacchioni, in preparation

Acknowledgments
The financial support by the European Union Seventh Framework Programme via the EU project DECORE (project 309741) under contract no. FP7-NMP-2012-SMALL-6 for Research and Technological Development is gratefully acknowledged.

Microsystems for Oxidative Stress Species Electrochemical Detection at the Level of a Cellular Population

Yun Li, Anne Meunier, Rémy Fulcrand, Catherine Sella, Laurent Thouin, Christian Amatore, Frédéric Lemaître, Manon Guille-Collignon

Ecole Normale Supérieure-PSL Research University, Chemitsry Department,
Sorbonne Universités - UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24,
rue Lhomond, 75005 Paris, France

manon.guille@ens.fr

In this work, we propose the detection of oxidative stress species with intrinsic benefits of electrochemistry and unprecedented progress in instrumentation where microelectrodes are playing prominent roles in the analysis of living cells behaviors.[1,2] Indeed, fabrication of Pt/Pt-black microband electrodes was first optimized to detect four ROS/RNS species (i.e., H_2O_2, $ONOO^-$, $NO^\bullet$, and NO_2^-) from macrophages. These electrodes were integrated into PDMS-glass microdevices in order to analyze these four key compounds released from cells populations. High analytical performances were evidenced according to the devices geometry and hydrodynamic conditions.[3] The control of the electrochemical responses by mass transport was validated through comparison with theoretical predictions. Simultaneous detections of ROS/RNS release from cells were then carried out under two different configurations of microdevices. Reproducible and statistically relevant results were obtained within only few experiments. These microdevices allow for easy characterizations of average behaviors of cells populations. This study paves the way to a very broad field of bioanalytical applications integrating electrochemical detections for high-throughput monitoring of living cells.[4]

[1] C. Amatore et al., Chem Rev, 2008, 108, 2585.
[2] Y. Wang et al., Microchim. Acta, 2010, 168, 177.
[3] C. Amatore et al., Anal. Chem., 2008, 80, 4976.
[4] Y. Li et al., Electroanalysis, 2013, 25(4), 895 ; Electrochimica Acta, 2014, 144, 111 ; Analytical and Bioanalytical Chemistry, 2015, *submitted*.

Corrosion protection of a carbon steel by water based epoxy coatings containing hydrotalcite intercalated with molybdate

To Thi Xuan Hang[1], Trinh Anh Truc[1], Nguyen Tuan Anh[1], Dinh Thi Mai Thanh[1],
Thai Hoang[1], Nadine Pebere[2]
[1]Institute for Tropical Technology, Vietnam Academy of Science and Technology
18 Hoang Quoc Viet, CauGiay, Hanoï, Vietnam
[2]Université de Toulouse, CIRIMAT, UPS/INPT/CNRS
ENSIACET, 4 Allée Emile Monso – CS 44362, 31030 Toulouse cedex 4, France
ttxhang@itt.vast.vn

Abstract

In recent years, ion exchangeable compounds such as clay montmorillonite or hydrotalcite for preparation of non-toxic anticorrosive pigments has been the subject of numerous investigations [1-4]. These ion-exchange compounds can be used for preparation of more friendly additives for storage and release of green corrosion inhibitors in organic coatings. In the present work, hydrotalcite intercalated with molybdate was prepared by co-precipitation method. Then, hydrotalcite containing molybdate (HTM) was incorporated in a water based epoxy coating at three concentrations (1 wt. %, 3 wt. % and 5 wt. %) for corrosion protection of a carbon steel. The HTM obtained was characterized by infrared spectroscopy, x-ray diffraction and scanning electron microscopy. Inhibitive action of HTM on carbon steel was examined by polarization curves and electrochemical impedance spectroscopy (EIS). The corrosion protection performance of the epoxy coatings containing HTM was evaluated by EIS, salt spray test and adherence test. It was shown that the molybdate was intercalated in the hydrotalcite structure and its loading was 11.5%. The polarization curves obtained on the carbon steel sample showed that the HTM is an anodic inhibitor. Its inhibition efficiency was around 94% at the concentration of 3 g/l. The presence of HTM in the water based epoxy coatings significantly improved the corrosion protection of the carbon steel. In the presence of a scratch in the coating, it was shown that the molybdate can be released from HTM and acted as corrosion inhibitor at the steel/coating interface.

References

1. Zheludkevich, ML, Poznyak, SK, Rodrigues, LM, Raps, D, Hack, T, Dick, LF, Nunes, T, Ferreira, MGS, "Active protection coatings with layered double hydroxide nanocontainers of corrosion inhibitor." *Corros. Sci.*, **52** 602-611 (2010).
2. Williams, G, McMurray, HN, "Inhibition of Filiform Corrosion on Polymer Coated AA2024-T3 by Hydrotalcite-Like Pigments Incorporating Organic Anions." *Electrochem. Solid-State Lett.*, **7** B13-B15 (2004).
3. Hang, TTX, Truc TA, Duong NT, Pébère, N, Olivier, MG, "Layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel." *Prog. Org. Coat.*, **74** 343-348 (2012)
4. Hang, TTX, Truc TA, Duong NT, Vu PG, Hoang, T, "Preparation and characterization of nanocontainers of corrosion inhibitor based on layered double hydroxides." *Appl. Clay Sci.*, **67** 18-25 (2012)

Keywords: hydrotalcite, molybdate, corrosion inhibitor, release, water based epoxy coating

Acknowledgments
This work was carried within the framework of the associated international laboratory "Functional Composite Material (FOCOMAT)" between France and Vietnam with the financial support of Centre National de la Recherche Scientifique (CNRS) and of Vietnam Academy of Science and Technology (VAST).

Linking the scales – Modelling Corrosion from 10^{-10}m to 10^{6}m

I.S.Cole[1], M.S.Venkatraman[1],M.Breedon[1] Clement Chu[1] W.Ganther[1] and Fiona Chen[1]
[1]*CSIRO Materials Science and Engineering, Private bag 33, Clayton South MDC, Victoria 3169, Australia*
Ivan.cole@csiro.au

This paper will present a multi-scale of corrosion that spans scales from molecular scale (where it considers the binding of inhibitor to metal surfaces) to the continental scale where it considers ocean production of marine aerosols and the aerosols subsequent transport across continents. Figure 1 highlights the models and the scales under which it operates. .

On active metals such as zinc and steel , multi-layers of oxide may develop. Adjacent to the metal surface a compact oxide is under particular circumstances observed. This compact oxide dramatically reduces the rate of metallic corrosion. Above, or in the absence of, the compact layer bands of porous oxide may develop with variable porosity from the metal or compact layer interface to the moisture layer. To model this porous oxide a porous oxide model has been developed. The porous oxide model (POM)is a continium model that accounts for diffusion, chemical and electrochemical process. In a system where the oxide is semi-conducting (such as zinc or iron) the oxide itself may support the oxygen reduction reaction (ORR). The POM considers the relative rate of the ORR at the metal surface and at the pore boundary (zincoxide/pore solution). The conditions generated within the porous layer will affect the conditions at the porous layer/compact layer interface and thus compact layer stability. Modelling of inhibitor/metal surface intercation is being undertaken to assess the components of molecular structure that lead to effective inhibition. In Figure 2 a model of the electronic configuartaion of a Na-4-mercaptobenzonate in an aqueous solution. These models are then linked with continuum models to predict the effective life of protective primers on aircraft in service

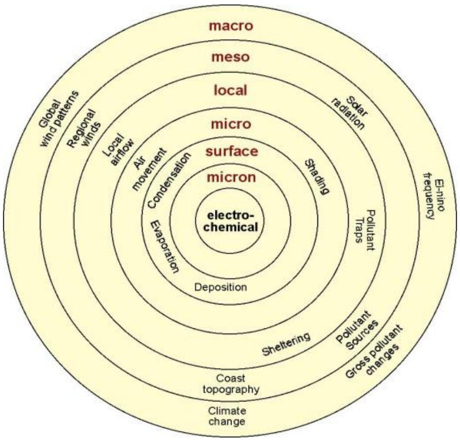


Figure 1. Framework For Multi-Scale model

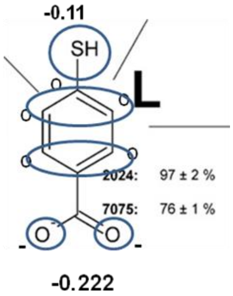


Figure 2 . Electronic Configuration of a Na-4-mercaptobenzonate in an aqueous

Analytical Study of Polarization Curve of Li-Air Battery based on Novel Products Deposition Model Suggested by First-Principles Molecular Dynamics Simulations

Wataru Yamamoto and Hiromitsu Takaba
Department of Environmental and Energy Chemistry, Graduate School, Kogakuin University
2665-1 Nakano, Hachioji, Tokyo 192-0015, Japan
bm14040@ns.kogakuin.ac.jp

1. Abstract

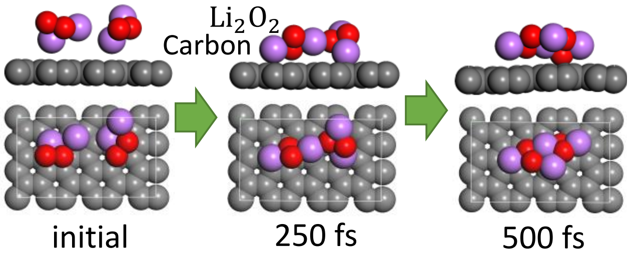
Li-air battery system achieves high specific energy density. There are, however, some challenge tasks must be overcome for commercialization. The most important issue is related to the pore clogging of air diffusion path by discharge products at the cathode. The main cathode discharge product is considered as Li_2O_2 and several models to explain the effect of deposition on discharge capacity has been reported [1]. However, deposition behavior of Li_2O_2 at atomistic level on cathode carbon surface is still obscure. In this study, we investigated Li_2O_2 deposition behavior on the carbon surface at atomistic level using first-principles molecular dynamics (FPMD). Moreover, we constructed analytical simulation model for evaluating a polarization curves for elucidating the relationship between atomistic deposition behavior and discharge capacity.

2. Method

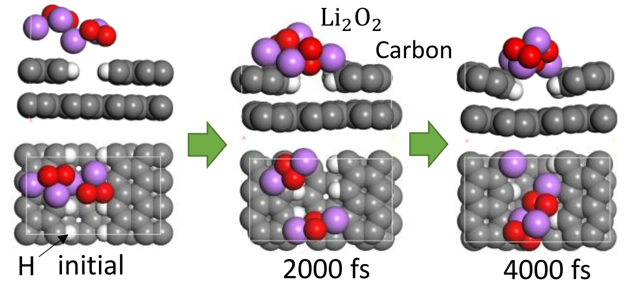
FPMD calculation was carried out with three-dimensional periodic boundary condition and density functional theory part employs using local density approximation with double numerical plus d function. Temperature in the dynamics was at 300 K. We considered the graphene like surface as a cathode carbon surface. We also calculated polarization curves using novel deposition model that is suggested from the result of FPMD calculation.

3. Results and Discussion

Li_2O_2 cluster was located on the carbon surface for FPMD calculation. Fig. 1 (a) shows that Li_2O_2 cluster is diffusing on the carbon surface and finally forms the larger cluster. Fig. 1(b) shows the FPMD result of H terminated graphite surface model that would be more realistic. In the beginning of the simulation, Li_2O_2 diffuses on the carbon surface similar to that of Fig. 1(a) and after some periods Li_2O_2 is clustering each other around the edge position of the carbon surface. In the same way, we also investigates the dynamics of Li_2O_2 cluster on the amorphous carbon surface model and elucidates that deposited Li_2O_2 diffuses on the surface and forms a larger cluster. In particularly, Li_2O_2 intends to gather around a carbon edge. From the result of FPMD calculation, we constructs a new edge model for discharge simulation based on Butler-Volmer equation. The effect of deposition pattern assuming that Li_2O_2 deposits around the edge of the carbon surface on the discharge capacity is investigated. It is elucidated that discharge capacity strongly depends on a carbon edge distribution. We also suggest an ideal carbon cathode structure for achieving high discharge capacity from our simulation results that will be presented at the conference.



(a) Graphite surface model



(b) Graphite surface with edge model

Fig. 1 FPMD results for products diffusion on the cathode surfaces.

[1] P. Andrei et al., J. Electrochem. Soc., **157**, 12, A1287 (2010).

A Chemical Approach to the Modelling of Band Gap of Passive Films for Corrosion Studies

F. Di Quarto, F. Di Franco, M. Santamaria

Electrochemical Materials Science Laboratory, DICAM University of Palermo, Viale delle Scienze,
90128 Palermo, Italy
francesco.diquarto@unipa.it

Photocurrent Spectroscopy (PCS) has gained a large consideration in the last decades as in situ technique for the characterization of semiconductors and photoconducting passive film/electrolyte junctions being able to provide information on the location of characteristic energy levels like: flat band potential (U_{fb}), internal photoemission threshold (E_{th}) and band gap value (E_g) (1-2).By taking into account that PCS is a non-destructive technique not demanding in terms of surface finishing, it appears evident why such a technique has becoming very attracting for corrosion studies (3). Moreover the possibility to use such a technique both in a macroscopic as well in a microscopic scale (1μm scale) has further enhanced the need to provide a quantitative approach to the use of experimental band gap data obtained in PCS experiment for deriving information on passive film composition.
At this aim we have shown, some years ago, that it is possible to correlate the band gap values of numerous binary oxide sand III-V Nitrides alloys to their composition by means of a semi-empirical approach (3) based on the use of the Pauling's equation for the average bond energy which could be written as:

$$E_g = 2[E_I(\chi_M - \chi_O)^2 + \Xi] \qquad (1)$$

where χ_M and χ_O are the electronegativities of metal and oxygen respectively and the remaining terms have been defined in the original work (3). On starting from eq. (1) we have shown, in previous works (4-6), that such a simplified approach is able to account for the band gap values of a large number of crystalline binary oxides and passive semiconducting film grown on metals and metallic alloys. In this work we will present some recent results, which support the use of PCS in a more quantitative way for getting out information on mixed ternary oxides, including sp,d mixed oxides of possible interest in corrosion studies.

1 - U. Stimming, Electrochim. Acta, **31**, 415 (1986)
2 - L. Peter, in "Comprehensive Chemical Kinetics", vol.**29**, p.382, Ed. by R.G. Compton, Elsevier Science, Oxford (1989)
3 - F. Di Quarto et al., J.Phys. Chem. B, **101**, 2519 (1997
4 -F. Di Quarto, C. Sunseri, S. Piazza, M. Santamaria, in "Handbook of Thin Films" Ed. H.S. Nalwa, Vol.**2**, pp 373-414, Academic Press (2002)
5 - F. Di Quarto, M. Santamaria, and C. Sunseri, in "Analytical Methods in Corrosion Science and Technology", P. Marcus and F. Mansfeld, Editors, p. 697, Taylor and Francis, Boca Raton, FL (2005).
6 - F. Di Quarto, F. La Mantia, M. Santamaria, in "Modern Aspects of Electrochemistry, No. 46: Progress in Corrosion Science and Engineering I", Ed. by Su-Il Pyun and Jomg-Won Lee, Ch. 4, p. 231, New York: Springer (UNITED STATES), 2009

Electrochemical Characterization of Various Diketopyrrolopyrrole Derivatives with Respect to HOMO/LUMO Energies

Tomáš Mikysek,[1] and Jiří Ludvík,[2]

[1] *Department of Analytical Chemistry, Faculty of Chemical Technology,University of Pardubice,*
Studentská 573, CZ-53210 Pardubice, Czech Republic, tomas.mikysek@upce.cz
[2] *J. Heyrovsky Institute of Physical Chemistry ASCR, v.v.i., Dolejškova 3, CZ-182 23*
Prague 8, Czech Republic.

Recently, solar cells (SC) based on bulk heterojunction (BHJ) architecture belong to one of the most promising organic photovoltaic (OPV) technologies [1]. While fullerene derivatives are successfully used as electron acceptors in these cells, a progress has been made in searching new and more efficient donors. One of the examined electron donors are compounds based on 3,6-diphenyl-2,5-dihydro-pyrrolo-[3,4-c]-pyrrole-1,4-dione (DPP) structure. Recently, some new derivatives were synthesized and tested for above mentioned application. In this contribution, some derivatives of DPP were electrochemically investigated and characterized using cyclic voltammetry (CV) and rotating disc voltammetry (RDV) at platinum electrode in non-aqueous media (acetonitrile/DMF) in order to estimate the respective reduction and oxidation potentials, to prove the reversibility of these electron transfers and stability of the radical intermediates, to determine electrochemically the HOMO-LUMO gap, to describe the influence of various substituents and to localize experimentally the first oxidation and first reduction center (that means the HOMO and LUMO orbitals) on the molecule.

From the CV and RDV experiments resulted that there are two reversible redox processes. In the structure, where two piperidine heterocycles are attached to both phenyl goups it has been found that the first oxidation process consumed two electrons (concerted) whereas the derivative with only one piperidine group showed only one-electron oxidation process as well as reduction processes in both derivatives. The oxidation has been also performed by chemical way (with $FeCl_3$) and the result was rather surprising when the oxidation showed to be stepwise [2]. The further experimental data interpretation was focused on influence of N-alkyl or N-ester substitution in pyrrole structure on first oxidation (HOMO) and first reduction (LUMO) processes. Both of the substitutions establish solubility of DPP derivatives in organic solvents. Whereas the length of alkyl chain does not play any important role in electrochemical behavior the ester is saving HOMO-LUMO gap but the shift in redox potentials is evident. The explanation of this manner can be found in rotation of phenyl groups due to the steric effect [3]. Based on these measurements it will be possible to find optimal substituents and thus to “tune” the properties of DPP derivatives for OPV applications.

Acknowledgements

The Ministry of Education, Youth and Sports of the Czech Republic, Project CZ.1.07/2.3.00/30.0021 “Enhancement of R&D Pools of Excellence at the University of Pardubice“, financially supported this work.

References

[1] Dou, L.; You, J.; Hong, Z.; Xu, Z.; Li, G.; Street, R.A.; Yang, Y., *Adv. Mater.* **2013**, *25(46)*, 6642-71.
[2] Luňák, S. Jr, Eliáš, Z., T. Mikysek, J. Vyňuchal, J. Ludvík, *Electrochim. Acta* **2013**, *106,* 351-359.
[3] David, J.; Weiter, M.; Vala, M.; Vyňuchal, J.; Kučerik, J. *Dyes Pigm.* **2011**, *89*, 137-143.

Photoelectrochemical evidence of inhomogeneous composition at nm length scale of anodic films on valve metals alloys

F. Di Franco[1], A. Zaffora, M. Santamaria[1], H. Habazaki[2], F. Di Quarto[1]

[1] Electrochemical Materials Science Laboratory, DICAM University of Palermo, Viale delle Scienze,
90128 Palermo, Italy
[2] Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan.
monica.santamaria@unipa.it

Amorphous and/or nanocrystalline oxide films can be easily prepared electrochemically by anodizing. The anodizing allows to grow oxides with structural and compositional features easily and strictly controlled by the process parameters. The choice of the growth conditions (i.e. current density and formation voltage) has a direct influence on the film thickness and on its crystalline or amorphous nature, while the electrochemical bath as well as the base alloy strongly affect the composition of the oxides. Concerning the electrochemical bath, it is important to consider the effect related to the possible incorporation into the oxide of species coming from the solution. In several papers [1-3], it has been reported that by anodizing some valve metal (i.e. Nb, Ta and Ti) in ammonium containing electrolytes, it is possible to incorporate nitrogen into the anodic films with a marked change in the optical properties of the oxides.

Starting from these experimental findings, in the present work we want to show how it is possible to induce N incorporation into anodic films few tens nm thick grown on Al-Ta and Nb-Ta alloys by anodizing such alloys in ammonium biborate solution (pH ~ 8.5). Impedance and photoelectrochemical measurements were performed in order to estimate dielectric constant, band gap, flat band potential and conductivity type of the anodic films prepared in ammonium free and ammonium containing solutions. According to differential admittance curves as well as according to the electrochemical impedance spectra N incorporation does not change appreciably the dielectric properties of the investigated anodic films. In contrast, the photoelectrochemical behavior is significantly influenced by the presence of nitrogen, which induces a redshift in the light absorption threshold of the anodic oxides and a change in the mobility of the photo-carriers.

The experimental findings derived from the photoelectrochemical characterization allowed suggest the formation of inhomogeneous films constituted by an inner N free layer and an outer N containing layer. The dependence of photocurrent on photon energy was rationalized in the frame of Butler – Gartner equation [4] as a function of the band gap and thickness of both layers. The fitting of the experimental data according to this bilayer model allowed to estimate the N penetration depth.

1 - S. Ono, K. Kuramochi, H. Asoh, Corros. Sci. 51 (2009) 1513.
2 - F. Di Franco, M. Santamaria, F. Di Quarto, E. Tsuji, H. Habazaki, Electrochimica Acta 59 (2012) 382-386.
3 - S. Miraghaei, M. Santamaria, F. Di Quarto, Electrochimica Acta 134 (2014) 150-158.
4 - F. Di Quarto, F. La Mantia, M. Santamaria, in: S.I. Pyun, J.W. Lee (Eds.), Modern Aspects of Electrochemistry, vol. 46, Springer, New York, 2009 (Chapter 4).

Catalytic activity of MN4 complexes adsorbed on carbon nanotubes towards oxygen reduction

C. Castro, N. Silva, M. Viera, C. Zúñiga, F. Tasca, F.J. Recio, J.H. Zagal
Departamento de Materiales. Universidad Santiago de Chile
Av. Libertador Bernardo O´Higgins 363. Santiago, Chile 9170022
francisco.recio@usach.cl

The ever expanding worldwide energy needs have made fuel-cells an important and permanent topic of research. However, their massive application in daily life has been hampered in part by the high cost of catalytic materials for the O_2 cathode that usually uses catalysts containing noble metals like Pt. Due to the high cost of Pt, most improvements are achieved by reducing the Pt loading for example by employing nanoparticles of Pt alloys. On the other hand, metallophthalocyanines and metalloporphyrins are well known as electrocatalysts for the reduction of O_2 (ORR) and have been extensively investigated (1), together with other similar molecules as “non-precious metal catalysts” with the aim of replacing Pt in fuel cells. Recent publications have shown that the catalytic activity of MN4 catalysts towards the ORR increases when the formal potential of the catalytic species (i.e. of the MN4 complex) and tends to the reversible potential of the ORR (2).

In this work several MN4 complexes (Fe and Co phthalocyanines and porphyrins) have been adsorbed on carbon nanotubes (CNT) (3). The study of catalytic activity for ORR has been performed in basic media. The results show the same trend reported before. When the catalysts are absorbed on CNT, a displacement to more positive values of the formal potential of catalyst is observed and related with the activity. The kinetic mechanism deduced by the Tafel slopes analysis does not change among the MN4 complexes adsorbed and non-adsorbed on CNT, indicating that the CNT support does not interfere with the reaction mechanism. The herein presented results are in line with those reported before where the catalytic activities increase when the formal potentials of the catalysts increase (more positive values)(2). However, an increase of almost two orders of magnitude of activity expressed as log i at constant potential is observed when the MN4 catalyst is adsorbed on CNT. This increase is not only an area effect. The activity increase is discussed and associated with a well ordered MN4 adsorption on the CNT surface.

1. J. H. Zagal, S. Griveau, J. Silva, T. Nyokong, F. Bedioui, *Coord.Chem. Revs* 254 (2010) 2755.
2. J.H. Zagal, F.J. Recio, C.A. Gutiérrez, C. Zúñiga, M.A. Páez, C. Caro. Electrochemistry Communications. 41 (2014) 24-26.
3. C.A. Gutiérrez, J.F. Silva, F.J. Recio, S. Griveau, F.Bedioui, C. Caro, J.H. Zagal. Electrocatalysis 5, 3 (2014)

Investigating transient phenomena in lithium ion batteries: a multiscale modeling approach

Trong-Khoa Nguyen, [1,2]† Abdelouahab El Kharbachi,[1,2] Kan-Hao Xue,[1,2] Matias Quiroga,[1,2] Dominique Larcher,[1,2,3] Alejandro A. Franco[1,2,3]ǂ
[1]*Laboratoire de Réactivité et Chimie des Solides - UMR CNRS 7314, Université de Picardie Jules Verne*
33 Rue Saint Leu, 80039 Amiens Cedex
[2]*Réseau sur le Stockage Electrochimique de l'Energie (RS2E) - FR CNRS 3459, France*
[3]*ALISTORE-ERI, European Research Institute, FR CNRS 3104, France*
† trongkhoa.nguyen@u-picardie.fr ǂ alejandro.franco@u-picardie.fr

The study of the response of Lithium Ion Batteries (LIBs) to fast transient power solicitations becomes nowadays a crucial topic in view of the emerging EV application of this technology. In this context LIBs are interconnected with an electrical engine, high dynamics power regulators and eventually with other electrochemical systems devoted to battery recharging [1]. One of the key aspects in the resulting transient response of LIBs is the ionic transport phenomena taking place at the interface between the liquid electrolyte and the solid active material (the so-called electrochemical double layer –EDL– region). In a recent publication, we have proposed a multiscale physical model describing the dynamical structure of such a nanoscale interface in response to an applied dynamical current density. This model, which deserves to be integrated into a fully multiscale cell model [2], allows capturing how the electrolyte composition (in terms of salt and solvent compositions) affects the electrode potential dynamics [3]. In that sense it goes beyond the prediction capabilities of classical EDL theories based on the Poisson-Nernst-Planck approach [4] or on the assumption of a constant double layer capacitance [1, 5].

In this work, a multiscale cell model including EDL has been developed to investigate the electrolyte relaxation effects in LIBs, i.e., the variation of cell potential when the discharge current is suddenly shut off. The numerical results are discussed and compared with dedicated in-house relaxation experiments. First, 4-electrode Li/Li_xFePO_4 cells with different electrolyte compositions (different amounts of DMC added into LP30 electrolyte, i.e., 1 mol/L $LiPF_6$ dissolved in a 1:1 weight-ratio EC/DMC solvent mixture) have been fully charged. Then, they have been discharged at a C/2 rate at room temperature until 50% state of charge, when we shut down the current and measured the potential dynamics upon relaxation (see Fig. 1a). From the good agreement between the experimental and the simulation results (Fig. 1b), new insights into the ionic transport processes at multiple spatio-temporal scales are provided.

Our study, carried out within the in-house multiscale simulation package MS LIBER-T, will open new perspectives on the understanding of the fast transient phenomena in LIBs.

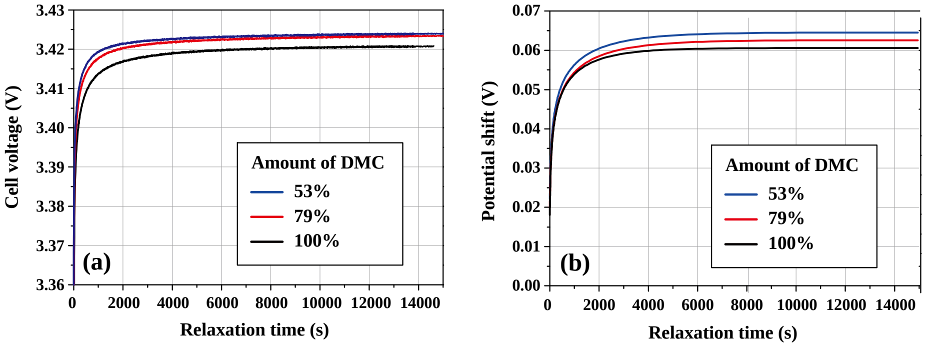


Figure 1. (a) Experimental relaxation curves with three different solvent mixtures; (b) Simulated cathode potential relaxation curves.

Acknowledgements

This work is funded by the French National Research Agency (ANR) through the project "ALIBABA".

References

[1] N. Legrand, S. Raël, B. Knosp, et al., *J. Power Sources* **251**, 370 (2014).
[2] A. A. Franco, *RSC Adv.* **3**, 13027 (2013).
[3] M. Quiroga, K.-H. Xue, T.-K. Nguyen, et al., *J. Electrochem. Soc.* **161**, E3302 (2014).
[4] A. A. Franco, P. Schott, C. Jallut, et al., *J. Electrochem. Soc.* **153**, A1053 (2006).
[5] J. Marcicki, A. T. Conlisk, G. Rizzoni, *J. Power Sources* **251**, 157 (2014).

A novel time-lapse microscopy technique to study the corrosion mechanisms and corrosion inhibitor effects during corrosion of Zinc Magnesium Aluminium (ZMA) alloys

Nathan Cooze[a1], James Sullivan[a2], Callum Gallagher[a], Thomas Lewis [a],
Tomas Prosek[b], Dominique Thierry[b]
[a] College of Engineering, Swansea University, Swansea SA2 8PP, UK
[b] Instituit de la Corrosion, 220 Rue Pierre Rivoalon, 2920 Brest, France
[1] 445376@swansea.ac.uk, [2] j.h.sullivan@swansea.ac.uk

The microstrucural corrosion mechanisms of three zinc-magnesium-aluminum (ZMA) alloy coated steels immersed in 1% NaCl pH 7 were observed using in-situ time-lapse optical microscopy, as shown in Figures 1.1 and 1.2. Preferential corrosion of the $MgZn_2$ lamellae within the eutectic phases was observed in all the ZMA alloys followed by subsequent dissolution of Zn rich phases. Image analysis software was used to measure the total extent and rate of corrosion. Scanning vibrating electrode technique (SVET) was used to estimate mass loss, which decreased as Mg and Al alloying additions were increased up to a level of 3 wt% Mg and 3.7 wt% Al. This was most likely due to the increased presence of MgO and Al_2O_3 at the alloy surface retarding the kinetics of cathodic oxygen reduction. The addition of a phosphate inhibitor in the form of 1×10^{-2} mol/dm^3 Na_3PO_4 to 1% NaCl pH 7 had a major influence on the corrosion mechanism for a ZMA alloy with passivation of anodic sites through phosphate precipitation observed using time-lapse. Intriguing rapid precipitation of filamentous phosphate was also observed and it is postulated that these filaments nucleate and grow due to super saturation effects. Polarisation experiments showed that the addition of 1×10^{-2} mol/dm^3 Na_3PO_4 to the 1% NaCl electrolyte promoted an anodic shift of 50mV in open circuit potential for the ZMA alloy with a reduction in anodic current of 2.5 orders of magnitude suggesting that it was acting primarily as an anodic inhibitor supporting the inferences from the time-lapse investigations. These phosphate additions resulted in a 98% reduction in estimate mass loss as measured by SVET demonstrating the effectiveness of phosphate inhibitors for this alloy system.

Figures

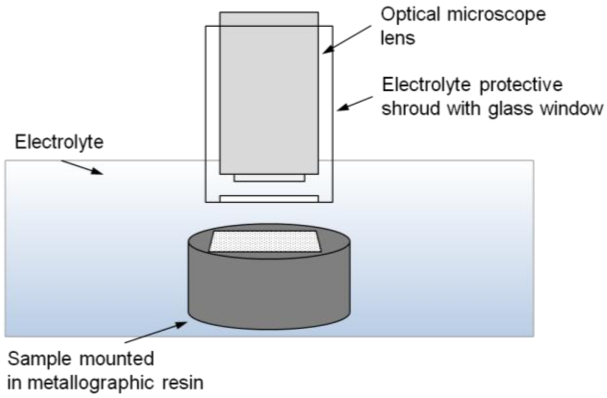


Figure 1.1: Schematic of time-lapse microscopy technique showing shroud to protect the microscope objective.

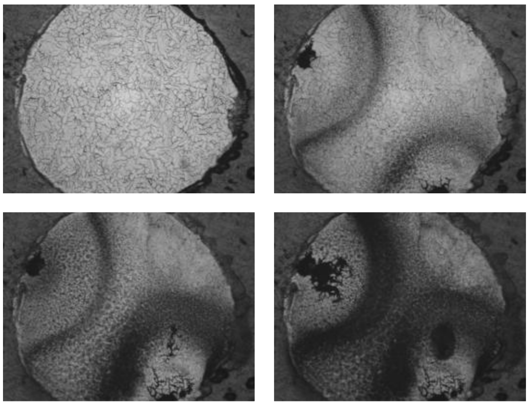


Figure 1.2: Time-lapse microscopy images during corrosion of 1%Mg-1%Al ZMA alloy in 1% NaCl at 3 hour intervals.

Presenting author. Tel.: +447949880539
Further co-authors' email addresses available on request

Scanning electrochemical microscopy with shearforce detection: some examples of application

Mathieu Etienne
LCPME UMR 7564 CNRS – Université de Lorraine,
405, rue de Vandoeuvre, Nancy, France
mathieu.etienne@univ-lorraine.fr

Recent advances in scanning electrochemical microscopy (SECM) are pushing the method towards new limits: scanning larger surfaces [1], with higher resolution [2], higher aspect ratio samples [3] or coupling the electrochemical data with additional chemical [4] and spectroscopic analysis [5].

For imaging experiments, the electrode-to-sample distance needs to be kept as constant as possible in order to analyze properly the heterogeneous reactivity of the sample. Microelectrode positioning, eventually achieved independently from the electrochemical measurement, has been the focus of considerable research since the early age of SECM [6].

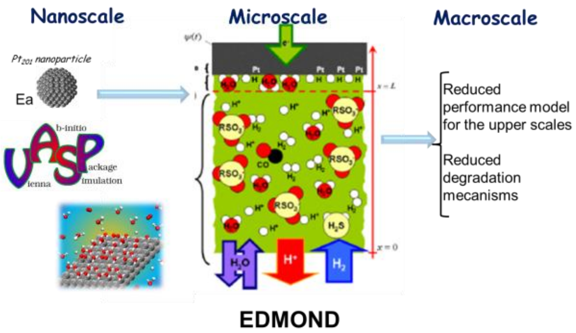
Shearforce detection was one of the first method to be successfully applied for non-electrochemical distance control in SECM [7]. It can be implemented with classic microelectrodes, without the need of micro/nanofabrication, where the only requirement is to have a flexible tip for actuation with a piezoelectric element [8]. Shearforce detection can be obtained with piezoelectric plates simply attached to the electrode body, a setup that allows a great flexibility [9-11].

Will be provided in this communication a discussion on the nature of the shearforce interaction with the analyzed substrate and some examples of application for micropatterning [12], kinetic analysis [10], corrosion studies [3,5], monitoring of the metabolic activity of bacterial cell layers in a water film [13], and evaluation of the photocatalytic activity of ultrathin TiO_2 layers.

[1] F. Cortés-Salazar, D. Momotenko, H.H. Girault, A. Lesch, G. Wittstock, Seeing big with scanning electrochemical microscopy, Anal. Chem. 83 (2011) 1493.
[2] M. Shen, R. Ishimatsu, J. Kim, S. Amemiya, Quantitative imaging of ion transport through single nanopores by high-resolution scanning electrochemical microscopy, J. Am. Chem. Soc. 134 (2012) 9856.
[3] M. Etienne, B. Layoussifi, T. Giornelli, D. Jacquet, SECM-based automate equipped with a shearforce detection for the characterization of large and complex samples, Electrochem. Commun. 15 (2012) 70.
[4] D. Momotenko, L. Qiao, F. Cortés-Salazar, A. Lesch, G. Wittstock, H.H. Girault, Electrochemical push-pull scanner with mass spectrometry detection., Anal. Chem. 84 (2012) 6630.
[5] M. Etienne, M. Dossot, J. Grausem, G. Herzog, Combined raman microspectrometer and shearforce regulated SECM for corrosion and self-healing analysis., Anal. Chem. 86 (2014) 11203.
[6] A.J. Bard, M. V. Mirkin, eds., Scanning Electrochemical Microscopy, Marcel Dekker Inc., New York, 2001.
[7] M. Ludwig, C. Kranz, W. Schuhmann, H.E. Gaub, Topography feedback mechanism for the scanning electrochemical microscope based on hydrodynamic forces between tip and sample, Rev. Sci. Instrum. 66 (1995) 2857.
[8] A. Hengstenberg, C. Kranz, W. Schuhmann, Facilitated tip-positioning and applications of non-electrode tips in scanning electrochemical microscopy using a shear force based constant-distance mode, Chem. Eur. J. 6 (2000) 1547.
[9] M. Etienne, J.-P. Moulin, S. Gourhand, Accurate control of the electrode shape for high resolution shearforce regulated SECM, Electrochim. Acta. 110 (2013) 16.
[10] M. Etienne, S. Lhenry, R. Cornut, C. Lefrou, Optimization of the shearforce signal for scanning electrochemical microscopy and application for kinetic analysis, Electrochim. Acta. 88 (2013) 877.
[11] C. Adam, F. Kanoufi, N. Sojic, M. Etienne, Shearforce positioning of nanoprobe electrode arrays for scanning electrochemical microscopy (SECM) experiments, *submitted.*
[12] Y. Guillemin, M. Etienne, E. Sibottier, A. Walcarius, Microscale Controlled Electrogeneration of Patterned Mesoporous Silica Thin Films, Chem. Mater. 23 (2011) 5313.
[13] D. Oulkadi, S. Banon, C. Mustin, M. Etienne, Local pH measurement at wet mineral-bacteria/air interface, Electrochem. Commun. 44 (2014) 1.

Multiscale Modeling of PEMFC: From Atomistic Calculations to Cell Performance and Degradation

Manuelle Quinaud[1], Pascal Schott[1], Mathias Gerard[1], Federico Calle-Vallejo[2], Rodrigo Ferreira de Morais[2], David Loffreda[2]
[1] *CEA/LITEN, Grenoble, France*
[2]*Laboratoire de Chimie, UMR CNRS 5182, ENS Lyon, France*
Manuelle.quinaud@cea.fr



Modeling and simulation techniques are becoming increasingly important both for understanding fundamental processes in fuel cells and for supporting design and optimization of fuel cell systems. It is well known that the various mechanisms involved in PEMFC are highly coupled, and these couplings must be taken into account in modeling to have a correct view of what happens in the cell. Therefore, the multi-scale methodology that is described in this work, and that corresponds to the objectives of the European project PumaMind is currently under quick development.

In this work, we focus on the multiscale by coupling atomic scale models, based on Density Functional Theory (DFT) calculations of the activation energy barriers (Ea) related to the reaction elementary steps (performed by the Theory group of ENS Lyon) [1-2] with a detailed Electrochemical Double Layer (EDL) model called EDMOND [3]. EDMOND is a physic oriented model based on a mechanistic approach that enables a direct coupling between the composition of the electrochemical interface and the kinetics of the reactions that occur on the Pt surface. EDMOND is a numerical implementation of the Transition State Theory without considering the equilibrium state and the associated “reversible potential” (as in the classical Bulter-Volmer approach). Therefore for each electrochemical reaction all of the reaction steps can be considered, using the DFT activation energies.

Performance and degradation can be easily coupled since both performance reactions like the Oxygen Reduction Reaction (ORR), and the degradation reactions (especially catalyst degradation: Pt dissolution and Ostwald ripening) take place at the EDL scale. Both reactions depend on the surface potential and the composition of the interface and both reactions have an influence on the electrochemical interface.

EDMOND is therefore well suitable for the simulation of the competition between the various mechanisms at the EDL scale. A reduced model can then be derived and integrated at the cell scale to consider the heterogeneities among the cell that impact the behaviour of the cell [4].

[1] Calle-Vallejo, *et al.*, *Angewandte Chemie International Edition*, Fast Prediction of Adsorption Properties for Platinum Nanocatalysts with Generalized Coordination Numbers, 54, (2014), 8316–8319.
[2] R. Ferreira de Morais *et al*., ACS Catalysis, 5 (2015), 1068-1077 , DOI: http://dx.doi.org/10.1021/cs5012525
[3] S. Passot. Etude expérimentale et par modélisation de l’impact d’impuretés de l’hydrogène sur le fonctionnement des piles à combustible à membrane échangeuse de protons (PEMFC). PhD thesis, Université de Grenoble, 2012.
[4] Robin *et al.*, *International Journal of Hydrogen Energy*, Multi-scale coupling between two dynamical models for PEMFC aging prediction. 38 (2013) 4675 – 4688.

Behavior of G-Quadruplex Forming DNA Oligonucleotides at Electrically Charged Surfaces of Mercury and Carbon Electrodes

Miroslav Fojta[1], Pavlina Vidlakova[1], Hana Pivonkova[1], Iva Kejnovska[1], Libuse Trnkova[2],
Michaela Vorlickova[1] and Ludek Havran[1]
[1]*Institute of Biophysics of the Academy of Sciences of the Czech Republic v.v.i.*
Kralovopolska 135, CZ-61265 Brno, Czech Republic
[2]*Department of Chemistry, Faculty of Science, Masaryk University*
Kamenice 5, CZ-62500, Brno, Czech Republic
fojta@ibp.cz

Electrochemical methods have been widely applied in nucleic acids (NAs) research. It has been well established that, particularly at the mercury electrodes[1], accessibility of nucleobase residues for electrode reactions, and thus electrochemical behaviour of the NAs, is strongly dependent on the DNA structure. In duplex DNA, the primary reduction site of cytosine is buried in the in the double helix interior making the Watson-Crick base-paired cytosine electrochemically silent, while the imidazole ring of guanine is relatively well-accessible via major groove to undergo a specific redox process at the hanging mercury drop electrode (HMDE) and yield peak G^{HMDE} even in the double stranded DNA. Similarly, primary oxidation of G giving rise to peak G^{ox} at carbon electrodes takes place at C8. When the guanine forms a Hoogsteen pair with protonated cytosine in $C•G•C^+$ triplex or with another guanine in C•G•G triplex[2] or in G-quadruplexes[3], the N7 atom is involved in hydrogen bonding and accessibility of the respective groups for reduction or oxidation at the electrodes is limited. Recently, oxidation of guanine residues involved in the G-quadruplexes formed by $(dG)_{10}$[4] or d(TGGGGT)[5] ODNs at glassy carbon electrodes has been reported to take place at a potential by about 100 mV more positive, compared to guanines in single-stranded ODNs, suggesting a more difficult electrode process in the case of the quadruplex structure[6].

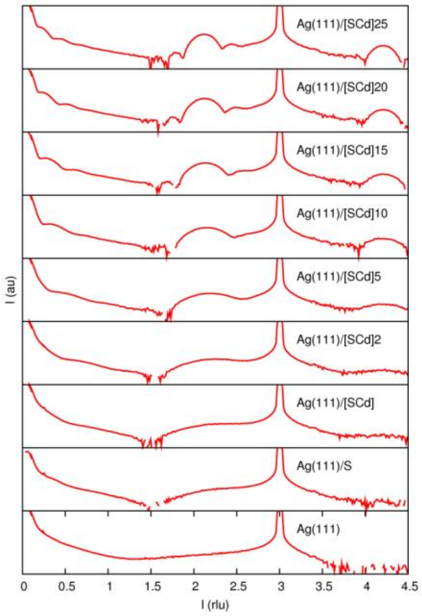
We studied effects of formation of G-quadruplex structures in central $(dG)_n$ segment in 15-mer ODNs (*G0* to *G15*), on their electrochemical and interfacial behaviour at the mercury and carbon electrodes. We observed strikingly different effects of the number of guanines in this segment on the height of peak G^{HMDE} measured at the HMDE and peak G^{ox} measured at the pyrolytic graphite electrode (PGE). While the intensity of the peak G^{ox} increased continuously between 1 and 15 guanines, the peak G^{HMDE} intensity increased with number of guanines up to *G5* and decreased sharply with further elongating $(dG)_n$ stretch. CD spectrophotometry and gel electrophoresis revealed formation of quadruplex structures for *G5* to *G15*. Starting from *G7*, these structures were remarkably resistant towards denaturing electrophoresis conditions. Cyclic voltammetry and alternating current voltammetry measurements suggest that the quadruplex structure formed by *G5* is at least partly disrupted at the HMDE, while structures formed by ODNs possessing longer $(dG)_n$ segments are stable in adsorbed state at the negatively charged mercury surface. Hoogsteen-paired guanine residues in the quadruplexes exhibit only limited accessibility for the reduction process at negatively charged surface of the HMDE, from which these rigid structures are repelled. On the contrary, the oxidation process of guanine at the PGE takes place at positively charged surface to which the ODN molecules are attracted, which facilitates oxidation of guanines even in the quadruplex structures.

[1] E. Paleček and M. Bartošík, *Chem Rev* **2012**, *112*, 3427-3481.
[2] a) X. H. Cai, G. Rivas, H. Shirashi, P. Farias, J. Wang, M. Tomschik, F. Jelen and E. Palecek, *Anal Chim Acta* **1997**, *344*, 65-76; b) E. Palecek, *Crit Rev Biochem Mol Biol* **1991**, *26*, 151-226.
[3] J. Kypr, I. Kejnovská, D. Renčiuk and M. Vorlíčková, *Nucleic Acids Res.* **2009**, *37*, 1713–1725.
[4] A.-M. Chiorcea-Paquim, P. V. Santos and A. M. Oliveira-Brett, *Electrochimica Acta* **2013**, *110*, 599-607.
[5] A. D. Rodrigues Pontinha, A.-M. Chiorcea-Paquim, R. Eritja and A. M. Oliveira-Brett, *Analytical Chemistry* **2014**, *86*, 5851-5857.
[6] A.-M. Chiorcea-Paquim and A. M. Oliveira-Brett, *Electrochimica Acta* **2014**, *126*, 162-170.

Understanding Electrochemical Layer by Layer Deposition: Order and Epitaxy in CdS Thin Films on Ag(111) Investigated by In-situ by Surface X-ray Diffraction

Francesco Carla', Andrea Magrini, Roberto Felici
ESRF-The European Synchrotron
CS40220 38043 Grenoble Cedex 9, France
carla@esrf.fr

Electrochemical Atomic Layer Epitaxy (ECALE) [1] has been demonstrated to be a very effective method for the production of thin films of semiconductor compounds with high grade of crystallinity [2-3]. This electrodeposition procedure is based on the alternate Under Potential Deposition (UPD) of different elements which allows the layer by layer growth of compounds on single crystal substrates.
UPD is a surface-limited phenomenon, for this reason the electrodeposition of an element in UPD conditions is generally limited to one atomic layer.
UPD processes on single crystals are not only dependent on the chemical nature of the substrate but also on its orientation [2], nevertheless the influence of the deposition conditions on the structure of the film is not clear. Aim of the present work was the in-situ characterization of the growth process of CdS thin films on Ag(111) in order to better understand the dynamics of the layer-by-layer growth process. In-situ structural characterization of thin films is generally a rather complex task as it requires high brilliance x-ray sources given the small thickness of the film, the high background of the electrochemical environment and the attenuation due to the presence of the solvent.
In-situ Surface X-ray Diffraction (SXRD) experiments were carried on the ID03 beamline at ESRF (Grenoble) using electrochemical flow cell specifically designed for this purpose. Even if it's well established that the sequential deposition of UPD layers of Cd and S on Ag(111) results in an ordered multilayer structure with lattice parameters comparable to the one of the wurtzite CdS structure [3], several aspects of the growth process were not yet fully understood. In-situ experiments allowed to record structural changes of the in-plane order and details of the out-of-plane relaxation of the film during the growth that could not be observed before. Moreover the dependency of the epitaxial order on the potential used for the UPD deposition process was also investigated.



X-ray reflectivity curves measured during CdS growth on Ag(111)

[1] B. W. Gregory and J. L. Stickney, J. Electroanal. Chem. 300, 1991, 543
[2] F. Carla', et al., J. Phys. Chem. C, 12, 6132 (2014)
[3] M.L. Foresti, et al. Electrochimica Acta, 51, 25, 5532 (2006)

Carbon Nanoelectrodes for Single-Cell Analysis: From Amperometric Sensing to Field-Effect Transistors

Jan Clausmeyer,[a] Yanjun Zhang,[b] Babak Babakinejad,[b] Miriam Marquitan,[a] Ainara López Córdoba,[b] Paolo Actis,[b] Yuri Korchev,[b] Wolfgang Schuhmann[a]
[a] *Analytische Chemie – Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Universitätsstrasse 150, D-44780 Bochum, Germany*
[b] *Department of Medicine, Imperial College London, London W12 0NN, United Kingdom*
jan.clausmeyer@rub.de

Analysis of single micro- or nanometric objects such as catalytically active nanoparticles or living cells reveals information not accessible to classical techniques for the study of their statistical ensembles. Carbon nanoelectrodes are a versatile platform for multiple sensor designs to perform non-ensemble measurements.

For the analysis of cell physiology on the single-cell level we report the functionalization of needle-type carbon nanoelectrodes with platinum as well as Prussian Blue to comprise sensitive amperometric nanosensors for the detection of oxygen[1] and hydrogen peroxide, respectively. Prussian Blue, the selective electrocatalyst for H_2O_2 reduction, was buried in etched nanocavities inside the carbon nanoelectrodes to prevent its detachment and dissolution. The amperometric probes were inserted into single living cells to measure biologically relevant oxygen species with minimal perturbation of the cell function due to the small dimensions of the probes.

Moreover, we report on the fabrication of highly sensitive field-effect transistor (FET) devices based on double-barrel carbon electrodes. By depositing polypyrrole (PPy) across the two individually addressable nanoelectrodes a conductive nanojunction was generated. The resulting FET device shows typical transistor behavior and sensitivity towards pH changes. Unlike most FET sensors, the needle-type design of these sensors allows for positioning the sensor in the microenvironment of cells and even for intracellular measurements.

References

(1) Actis, P.; Tokar, S.; Clausmeyer, J.; Babakinejad, B.; Mikhaleva, S.; Cornut, R.; Takahashi, Y.; López Córdoba, A.; Novak, P.; Shevchuck, A. I.; Dougan, J. A.; Kazarian, S. G.; Gorelkin, P. V.; Erofeev, A. S.; Yaminsky, I. V.; Unwin, P. R.; Schuhmann, W.; Klenerman, D.; Rusakov, D. A.; Sviderskaya, E. V.; Korchev, Y. E. *ACS Nano*. **2014,** *8*, 875–884.

(2) Clausmeyer, J.; Actis, P.; López Córdoba, A.; Korchev, Y. E.; Schuhmann, W. *Electrochem. Commun.* **2014**, *40*, 28–30.

The role of surface/volume ratio on electrochemical phase transformation reactions taking place at nano/micro-structured electrodes

D. Fernández, L. Romeral, M.E.G. Lyons
Trinity College Dublin, School of Chemistry & CRANN/AMBER,
College Green, Dublin 2, Ireland
dafernan@tcd.ie

In the electrochemistry of nano/micro-structured materials, the assumption of continuum is no longer valid, as it is now expected that properties are non-uniform between two specific points. In particular, around a nano/micro-structured active site, due to the large surface/volume ratio, surface forces such as the electrostatic force and fluid damping become predominant.

At the same time, the material is usually characterized using techniques and concepts that take into account a much larger scale. The properties of nano/micro-structured materials vary in space from the subatomic scale up to the mm scale, where strongly coupled, multiscale and multiphysical-chemical problems are present. Therefore it is important to address and understand what is the actual effect of surface/volume ratio on the electrochemical reactions. This is of particular importance for phase transformation reactions, where high supersaturation values can be easily achieved and also strong couplings between the electric, fluidic and/or thermal fields appear to co-exist in the laws describing them. Furthermore, these aspects must be taken into account for a proper scaling up for industrial applications such as Electrowinning or Fuel Cells if nano/micro-structured materials are examined for those purposes due to its unique properties.

In this work, we compare phase transformation reactions taking place at electrodes of different size spanning four orders of magnitude, from micro to the cm scale, at comparable nominal rates, and examine the different responses. Hydrogen and Oxygen Evolution Reactions as well as Metal Electrodeposition are examined as relevant examples that may have an importance for Electrowinning and Fuel Cells industrial applications. The surface/volume ratio given by the actual active site and its surroundings is analysed under the light of voltage-current responses, and the role of supersaturation is discussed.

Probing the Mechanical Deformation of 2D Metal Carbides upon Cation Intercalation at the Nanoscale.

Jeremy Come,[a] Jennifer Black,[a] Michael Naguib,[a] Maria Lukatskaya,[b] Majid Beidaghi,[b] Sergei Kalinin,[a] Yury Gogotsi,[b] and Nina Balke[a]
[a]*Center for Nanophase and Materials Science, Oak Ridge National Laboratory,* Oak Ridge, TN, 37831, USA
[b]Department of Materials Science and Engineering & A. J. Drexel Nanotechnology Institute, Drexel University, Philadelphia, PA, 19104, USA
comeje@ornl.gov

The titanium carbide $Ti_3C_2T_x$ (where T_x stands for termination functions at the surface such as –OH, =O, and –F) is a member of the recently discovered family of two-dimensional (2D) materials known as MXenes.[1] This material demonstrates a high intercalation capacitance related to the rapid transport of ions within the structure, making this a promising electrode material for supercapacitors.[2] To date however, the intercalation mechanism is poorly understood and other techniques able to probe the dynamics are required. In this work, *in-situ* Atomic Force Microscopy is used to monitor the strain developed in a $Ti_3C_2T_x$ electrode during intercalation/extraction of monovalent and divalent cations in a variety of aqueous electrolytes (Fig.1A-C). The actuation mechanism was found to be strongly dependent on the ion charge and ionic radius. The electrode undergoes a large contraction during Li^+, Na^+ or Mg^{2+} intercalation, whereas intercalation of larger cations such as K^+ lead to a slight expansion (Figs.1D-E). The unique mechanical changes induced by the presence of cations between the layers were probed by Band-Excitation PFM using photothermal cantilever excitation. Spatial mapping of the resonance frequency (Fig.1F) showed that the elastic modulus of the carbide increases when Li^+ ions are intercalated in good agreement with the strong interactions between MXene sheets that leads to contraction.

These results are exciting because they shed light on the cation intercalation mechanism in the 2D structure of the carbide, and its outcome on the mechanical deformation. Moreover, the interactions between cations and the carbide layers can be efficiently probed with PFM techniques.

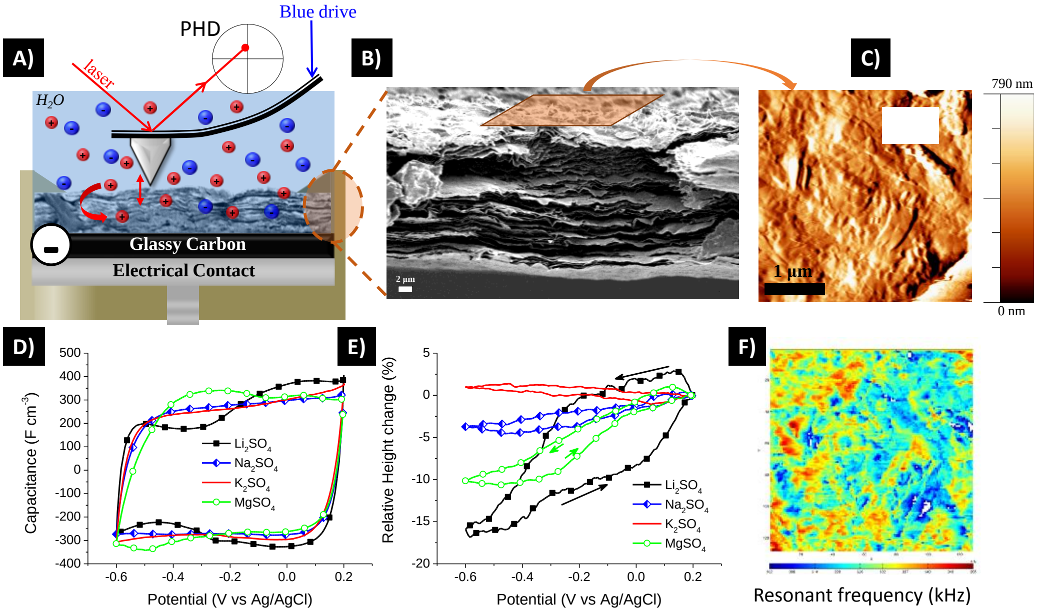


Figure 1: A) Schematic representation of the experimental setup, B) SEM image of the MXene electrode, C) AFM image of the MXene surface, D) CV curves of MXene at 2mV/s in different electrolytes and E) Corresponding relative electrode deformation, F) Resonance frequency in Li_2SO_4 electrolyte obtained by Band-Excitation PFM at 0V vs Ag/AgCl.

---

[1] M. Naguib *et al.*, *Advanced Materials* **2011**, *23*, 4248-4253.

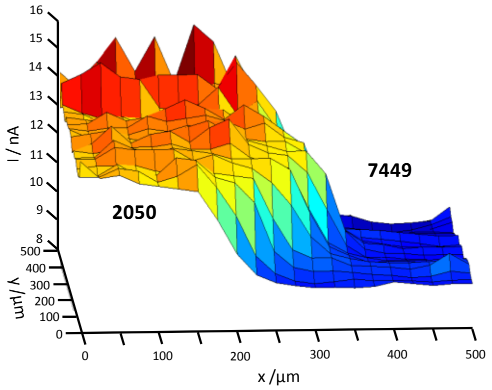
[2] M. Lukatskaya *et al.*, *Science* **2013**, *341*, 1502-1505.

Comparison between SECM and LEIS measurements in the study of FSW alloy assembly

O. Devos 1,), E. Bousquet 1), M. El May 2), T. Palin-Luc 3), A. Poulon-Quintin 4), M. Puiggali 1),
N. Saintier 3), D. Sidane 1), M. Touzet 1), V. Vivier 5)

1) Université Bordeaux, I2M, UMR 5295, 351 Cours de la Libération 33405 Talence - France
2) CNRS, I2M, UMR 5295, 33405 Talence - France
3) Arts et Metiers ParisTech, I2M, UMR 5295, 33405 Talence - France
4) Université de Bordeaux, ICMCB, UPR 9048, 87 Avenue du Dr Schweitzer, 33608 Pessac - France
5) Université Pierre et Marie Curie, LISE, UMR 8235, 4 Place Jussieu, 75252 Paris cedex 05 - France

The friction stir welded (FSW) assembly of 2050-T8 and 7449-T79 was studied by local electrochemical techniques, namely SECM and LEIS, under non corrosive and low corrosive conditions. During the FSW process, it generates different well defined microstructural zones giving rise to a galvanic coupling at their interfaces [1]. We propose to investigate local electrochemical reactivity on a 2050/7449 friction stir welded material with the scanning electrochemical microscope (SECM). The nugget interfaces of the dissimilar 2050-T8 / 7449-T79 FSW welded joint is also be investigated with local electrochemical impedance spectroscopy (LEIS) [2-4] This technique was shown to be useful for describing the galvanic coupling between two adjacent domains [5-7]. For instance, Al-Cu/Al-Cu-Mg model alloy was successfully investigated to mimic the electrochemical behavior of the Al2CuMg particles in the 2024 Al alloy [8]. The SECM experiments were carried out in a non corrosive media to study the electrochemical kinetics directly on the passive film above the different microstructural zones, whereas the LEIS was performed in a slightly corrosive environment to highlight the electrical and electrochemical interactions between the different domains. The results are also correlated with those obtained from the FSW material under corrosive environment [9].



3D-SECM image of the interface in the nugget domain formed
by FSW 2050-T8 / 7449-T79 in 10 mM $K_4[Fe(CN)_6]$ $3H_2O$ + 0.5 M K_2SO_4

References

[1] E. Bousquet, A. Poulon-Quintin, M. Puiggali, O. Devos and M. Touzet, Corros. Sci., **53** (2011) 3026
[2] R.S. Lillard, P.J. Moran and H.S. Isaacs, J. Electrochem. Soc., **139** (1992) 1007
[3] V.M.-W. Huang, S.-L. Wu, M.E. Orazem, N. Pebere, B. Tribollet and V. Vivier, Electrochim. Acta, **56** (2011) 8048
[4] I. Annergren, D. Thierry and F. Zou, J. Electrochem. Soc., **144** (1997) 1208
[5] J.B. Jorcin, C. Blanc, N. Pebere, B. Tribollet and V. Vivier, J. Electrochem. Soc., **155** (2008) C46
[6] L. Lacroix, C. Blanc, N. Pebere, B. Tribollet and V. Vivier, J. Electrochem. Soc., **156** (2009) C259
[7] C. Blanc, N. Pebere, B. Tribollet and V. Vivier, Corros. Sci., **52** (2010) 991
[8] L. Lacroix, C. Blanc, N. Pebere, G.E. Thompson, B. Tribollet and V. Vivier, Corros. Sci., **64** (2012) 213
[9] E. Bousquet, O. Devos, M. Puiggali, M. Touzet, V. Vivier, A. Poulon-Quintin, Journal of the Electroanalytical Chemistry, **737** (2015) 206

Multiscale electrochemical-thermal modeling of cylindrical Li-ion cells and comparison with electrochemical-calorimetric studies

C. Ziebert[1], A. Melcher[1], A. Ossipova[2], B. Lei[1], M. Rohde[1], H. J. Seifert[1]
[1]*Karlsruhe Institute of Technology, Institute of Applied Materials-Applied Material Physics*
Hermann-von-Helmholtz-Platz, 76344 Eggenstein-Leopoldshafen, Germany
carlos.ziebert@kit.edu
[2]*Ruprecht-Karls University Heidelberg, faculty of physics and astronomy, Germany*

Based on the general geometrical structure of a Li-ion battery the mathematical and physical modeling of the underlying electrochemical and thermal processes which govern the time and spatial dynamic behavior must take different length scales into account. In a top-down approach a Li-ion battery can be decomposed mainly in three physical domains, the cell, the electrode and the particle domain (Fig. 1). In this so-called multi-scale-multi-domain (MSMD) model at each domain the occurring physical processes are governed by certain state variables which depend on the state variables of the other domains.

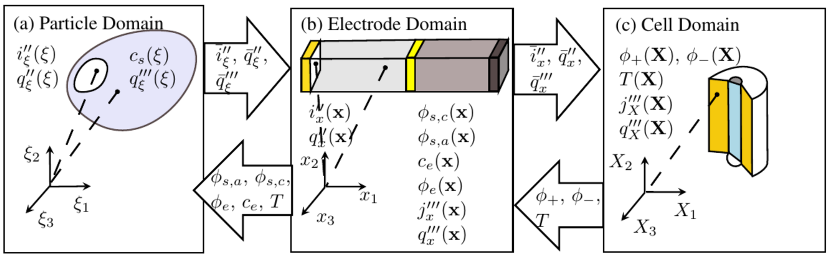


Fig.1: Model variables in each domain and corresponding coupling in the Multi-Scale-Multi-Domain (MSMD) model

On each domain the governing partial differential equations and algebraic equation for each state variable will be introduced. This results in a coupled system of parabolic and elliptic partial differential equations for the concentration of Li-ions in the solid and liquid phase, electric potentials and temperature respectively. Furthermore the homogenization of volumetric and surface current and heat densities are discussed as well as the proper determination of material properties from measurements with respect of the porous structure of a battery. This theroretical approach has been implemented in COSMOL Multiphysics. As input data available structural and thermophysical data have been used.

In parallel measurements of the thermal behavior have been performed for different cylindrical cells in an accelerating rate calorimeter (ES-ARC, Thermal Hazard technology with integrated battery cycler). Both isoperibolic investigations at specific temperatures in the range from 25 to 60 °C and adiabatic measurements were performed. For the temperature behavior a good qualitative agreement between the simulation and the experimental results was found for both environmental conditions. Fig. 2 shows the comparison between a simulation and a measurement for 0.5 C charge and discharge rate for a cylindrical 18650 cell with $LiMn_2O_4$ cathode and graphite anode. In future such comparisons will help to improve the thermal management of the cells and prevent them from going into thermal runaway.

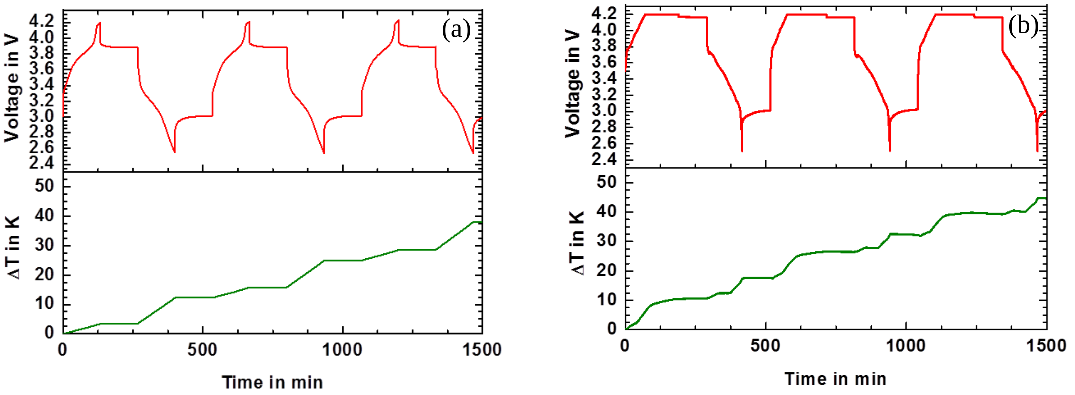


Fig.2: Comparison of simulation (a) and experimental results (b) for 0.5 C charge and discharge rate for a cylindrical 18650 cell with $LiMn_2O_4$ cathode and graphite anode

A numerical method for Nernst-Planck-Poisson Systems with volume constraints

Jürgen Fuhrmann, Christian Merdon
Weierstrass Institute for Applied Analysis and Stochastics
Mohrenstrasse 39, 10117 Berlin, Germany
juergen.fuhrmann@wias-berlin.de

Recent developments in electrochemical modeling have lead to an increased interest in numerical simulations of electrolytic systems which are able to resolve the polarization boundary layer. Classically, the problem is formulated based on the Nernst-Planck-Poisson system for ion transport in a self-consistent electrical field. Various model improvements are currently discussed in order to take into account the volume constraint for solute concentrations and solvation effects, see e.g. [1,2,3,4].

The talk reviews a successful finite volume discretization strategy from semiconductor analysis [5,6] and discusses problem reformulations which allow for its application in the context of electrolyte modeling based on the improved Nernst-Planck equations. Special emphasis is made on the proper reflection of qualitative properties of the physical model at the discrete level [7,8]. Along with calculation results for benchmark examples, the influence of various model improvements is demonstrated.

[1] V. Freise. Z. Elektrochemie, Ber. Bunsenges. für phys. Chemie 56.8 (1952): 822-827.

[2] M. Z. Bazant, B. D. Storey, A. A. Kornyshev, Phys. Rev. Lett. 106, 046102 (2011)

[3] W. Dreyer, C. Guhlke, R. Müller, Phys. Chem. Chem. Phys. 15, 7075 – 7086 (2013)

[4] W. Dreyer, C. Guhlke, and M. Landstorfer. Electrochem. Comm. 43 (2014): 75-78.

[5] D. L. Scharfetter, H. K. Gummel, IEEE Trans Electron. Dev. 16, 64-77 (1969)

[6] K. Gärtner, SIAM J. Sci. Comput. 31, 1347-1362 (2009)

[7] M. Bessemoulin-Chatard, Numerische Mathematik 121, 637-670 (2012)

[8] J. Fuhrmann, WIAS preprint No. 1943 (2014)

Inverse Modeling of Thin Layer Flow Cells for Detection of Solubility, Transport and Reaction Coefficients from Experimental Data

Jürgen Fuhrmann[1], Alexander Linke[1], Christian Merdon[1], Timo Streckenbach[1], Mehdi Khodayari[2],
Helmut Baltruschat[2]

[1] *Weierstrass Institute for Applied Analysis and Stochastics*
Mohrenstrasse 39, 10117 Berlin, Germany
juergen.fuhrmann@wias-berlin.de

[2] *Institute of Physical and Theoretical Chemistry, University of Bonn*
Römerstr. 164, 53117 Germany

Thin layer flow cells are used in electrochemical research as experimental devices which allow to perform investigations of electrocatalytic surface reactions under controlled conditions with reasonably small electrolyte volumes. Moreover, they are used for coupling electrochemistry to an on-line product analysis such as differential electrochemical mass spectrometry (DEMS).

State of the art interpretation of experimental data is based on the determination of transfer coefficients using auxiliary measurements with known characteristics by analogy to the detection of products at the ring of a rotating ring-disc-electrode. Extrapolation of data to the limit cases of infinite flow rates or very low flow rates is often necessary, but requires a variation of the flow rates over three orders of magnitude. Although often successful, this approach is limited to rather simple systems and reactions.

This paper updates the achievements from [2] and suggests a more general approach by an accurate numerical simulation of the flow (by finite element methods) and the coupled transport and reaction processes in the flow cell (by finite volume methods). Some new modifications to the coupling based on [1] result in a stable, efficient, convenient method that is guaranteed to comply with the physical bounds. In order to perform parameter identification, the simulation tool is coupled to standard optimization tools.

After an assessment of the inverse modelling approach using known realistic data, first results of the identification of solubility and transport data for O_2 dissolved in organic electrolytes are presented.

[1] Linke, A. (2014). On the role of the Helmholtz decomposition in mixed methods for incompressible flows and a new variational crime. *Computer Methods in Applied Mechanics and Engineering*, *268*, 782-800.

[2] Fuhrmann, J., Linke, A., Langmach, H., & Baltruschat, H. (2009). Numerical calculation of the limiting current for a cylindrical thin layer flow cell. *Electrochimica Acta*, *55*(2), 430-438.

New insights in the electronic transport in reduced graphene oxide using Scanning Electrochemical Microscopy

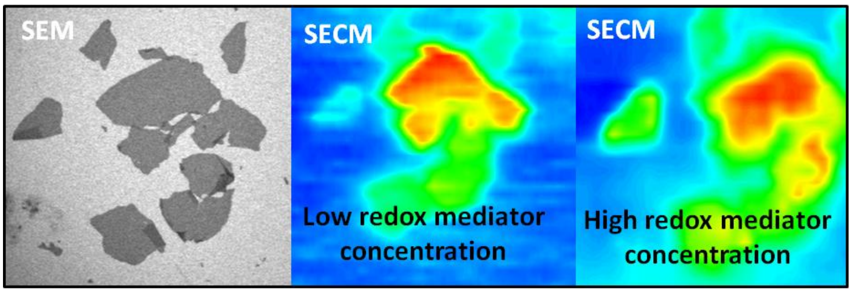
T. Bourgeteau, S. Le Vot, M. Bertucchi, V. Derycke, B. Jousselme, S. Campidelli, R. Cornut
CEA Saclay, IRAMIS, NIMBE (UMR 3685), LICSEN
Gif-sur-Yvette Cedex F-91191, France
renaud.cornut@cea.fr

Graphene and graphene analogues such as GO or reduced-GO (r-GO) are attracting increasing attention from the scientific community.[1] These materials have outstanding properties, so that many potential applications in the fields of electronics, sensors, catalysis and energy storage are being considered. GO combines several advantages such as availability in large quantity, low cost and easy processability. However, contrary to graphene, GO is electronically insulating and has to be reduced into a conductive material, r-GO.

In a recent work[2] we introduced a new localized functionalization method of GO deposited on a silicon oxide surface based on its reduction at the local scale thanks to scanning electrochemical microscopy (SECM): the reducer is generated at the microelectrode, that is moved close to the substrate. The recovery of electronic conductivity upon reduction enables the selective electrochemical functionalization of patterns.

In the present work, we introduce a new method to evaluate at a local scale the conductivity of r-GO layers with SECM.[3] In addition we show how images of individual and interconnected flakes directly reveal the signature of the contact resistance between flakes in a non-contact and substrate-independent way.[4] Quantitative evaluation of the parameters is achieved with the support of numerical simulations to interpret the experimental results.

Overall, these works illustrates the high potential and versatility of SECM to investigate and functionalize 2D materials.



Presentation of the combined SEM-SECM responses at the basis of the advanced electronic conduction characterization.[4]

(1) Geim, A. K. *Science* **2009**, 324, 1530.
(2) Azevedo, J.; Fillaud, L.; Bourdillon, C.; Noel J.-M.; Kanoufi F.; Jousselme B.; Derycke V.; Campidelli S.; Cornut R. *J. Am. Chem. Soc.*, **2014**, 136, 4833.
(3) Azevedo, J.; Bourdillon, C.; Derycke, V.; Campidelli, S.; Lefrou, C.; Cornut, R. *Anal. Chem.* **2013**, 85, 1812.
(4) T. Bourgeteau, S. Le Vot, M. Bertucchi, V. Derycke, B. Jousselme, S. Campidelli, R. Cornut, *J. Phys. Chem. Lett*, **2014**, 5, 4162.

Multiscale Modelling of Porous Electrodes in Semi-Solid Flow Batteries

Kudakwashe Chayambuka, Xochitl Dominguez-Benetton *
Separation and Conversion Technology, Flemish Institute for Technological Research
Boeretang 200, 2400 Mol, Belgium
** xoch@vito.be*

Semi-solid flow batteries (SSFB) are a novel technology for energy storage which combines the high energy density of Li-ion batteries with the flexible system architecture and low costs of redox flow batteries. SSFB may potentially address both grid-scale and transportation scale energy needs [1]. Flowable micro-scaled particles are employed as the active electrode material—which are suspended in the electrolyte together with a load of porous nano-scaled carbon particles and an active material which achieves faradic energy storage [2]. The electrochemical interfaces of SSFB are the object of study of the European FP7 project InFluENCE [3]. Part of the project and the present work aim to develop a tool for modelling SSFB at multiscale level using COMSOL Multiphysics®. The blend of electrolyte with flowable micro-scaled electrodes and nano-scaled carbon can be approximated as a porous domain at flow steady state conditions, wherein the electrolyte and the nano-scaled carbon constitute a continuum and the active electrode particles are taken as separate domains. The mathematical modelling of such kind of phenomenon presents complications arising from the different length and time scales at which the electrochemical processes occur. The present work featured either stationary or flowing electrodes, simultaneously allowing the analysis of the continuum and the micro-scale solid active particles.

A tertiary current distribution model for the porous electrode was combined with a study of diffusion for chemical species (i.e. Li^+) in the micro-scale active particles. The 1D cell geometry was set separate to the active particle geometry and both were coupled using the general extrusion operators. The results of this coupled model were compared to results arising from a model based on the work of Newman et al [4]. Using this approach the battery voltage and concentrations were determined. The values were in good agreement with those obtained in similar model predictions. Our model however goes a step further to analyse the evolution of the solid phase properties at different coordinates. This offers greater flexibility to the model in the study of multiple phenomena which can occur on the surfaces of the active particles without trading off the full cell effects.

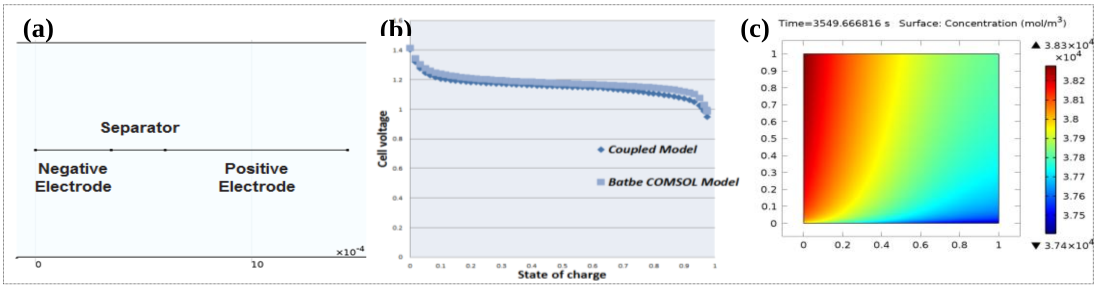


Figure 1: Some of the results obtained from the separate phases of 1D model. (a) The full cell domain (b) The cell voltage as a function of state of charge, (c) Positive active particle surface and internal concentrations.

The potential of multiphysics, multiscale modelling is further being exploited in a 2D whole cell flow channel to study the evolution of the state of charge at the inlet and outlet boundaries of SSFB with the purpose to design optimized interfacial layers though chemical and morphological optimization of active materials. Upon combination with experimental data, the modelling tool presented here can be also useful to derive scale-up parameters and to perform mass and charge balances, among other possibilities.

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 608621. Yolanda Alvarez-Gallego (VITO) and Daniel Buchholz (KIT-HIU) are acknowledged for their valuable discussions.

References

[1] Duduta M *et al.* (2011) *Adv Energy Mater* **1**(4):511–516.
[2] Hatzell KB, Boota M, Kumbur EC, Gogotsi Y (2015) J Electrochem Soc **162**(5):A5007–A5012.
[3] http://fp7-influence.eu/node/1
[4] Paxton B and Newman J (1997) *J Electrochem Soc* **44**:3818–3831.

Three-dimensional transient modeling of non-aqueous electrolyte lithium-air battery

Geonhui Gwak, Hyunchul Ju
Department of Mechanical Engineering, Inha University
100 Inha-ro, Nam-Gu Incheon 402-751, Republic of Korea
hcju@inha.ac.kr

A three-dimensional transient model for a non-aqueous electrolyte lithium-air battery is developed to numerically investigate key physical and transport phenomena for the discharging. The proposed model rigorously considers lithium peroxide (Li_2O_2) formation and evolution in the cathode electrode, and their complicated interactions with mass transport and electrochemical reactions. The proposed model is validated against experimental data [1] measured with polyvinylidene fluoride-hexafluoropropylene (PVDF) cathode at 0.1 mA/cm^2. In addition, detailed simulation results, including multidimensional contours, clearly elucidate the discharging behavior of a non-aqueous electrolyte lithium-air battery under different cell designs and operating conditions. We suggest that the proposed model could aid in the development of optimal operating strategies.

References

[1] J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, D. Foster, J. Electrochem. Soc. 150 (2003) A1351.

Presenting author data

Postal address : Department of Mechanical Engineering, Inha University, 100 Inha-ro, Nam-Gu Incheon 402-751, Republic of Korea

Phone : +82-32-873-7312

Fax : +82-32-868-1716

e-mail : Gwak.geonhui@inha.edu

Corresponding author data

Postal address : Department of Mechanical Engineering, Inha University, 100 Inha-ro, Nam-Gu Incheon 402-751, Republic of Korea

Phone : +82-32-860-7312

Fax : +82-32-868-1716

e-mail : hcju@inha.ac.kr

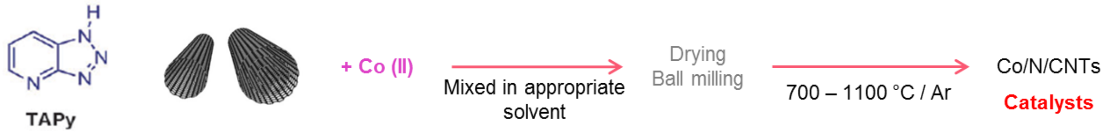
Electrochemical and Physico-Chemical Investigation of New Promising N-Functionalized Carbon Nanotubes for Oxygen Reduction Reaction

S. Le Vot, G. Laffay, B. Jousselme
CEA Saclay, IRAMIS, NIMBE (UMR 3685), LICSEN
Gif-sur-Yvette Cedex F-91191, France
steven.le-vot@cea.fr

Polymer electrolyte membrane fuel cell (PEMFC) is a very promising technology that could be used for electrical transportation and/or as a stationary energy supplier (e.g. domestic applications). In such devices, chemical reactions that lead to the production of an electric current involve the oxidation of hydrogen (HER) at the anode and the reduction of oxygen (ORR) at the cathode. PEMFC operate under acidic conditions and unfortunately the conventional catalysts currently used for O_2 reduction as for H_2 oxidation are based on Pt which is scarce and very expensive. In order to meet the industrial requirements, and particularly when electrical vehicle applications are targeted, development of new efficient catalysts that could replace platinum is crucial [1].

Nitrogen-doped carbon nanotubes (NCNTs) are low cost promising alternative materials in fuel-cell catalysis [2]. We recently demonstrated that such compounds could compete with platinum in alkaline media [3] but unfortunately electrochemical activities remains unsatisfying in acidic media [4]. Thus, in order to enable a practical application of NCNTs materials (i.e. to be the closest of the performances reached with Pt), new synthetic methods must be developed allowing to obtain structural and architectural features providing enhanced electrochemical performances (high electrocatalytic activity, good stability and resistance to corrosion).

We report herein the synthesis [5] and the characterizations at different length scale of promising catalysts for the ORR prepared through the annealing treatment under inert conditions of a carefully chosen azole derivative, used as nitrogen precursors, supported on multi-wall carbon nanotubes.



Scheme 1: Method for preparing N-functionalized CNTs catalysts

This project involves advanced electrochemical analysis of the performances, combined with BET (macroscopic external surface as well as microporosity), XPS (atomic composition), SEM (macro-scale morphology) and TEM (nano-scale morphology). It leads to a better understanding of the performances (electrocatalytic activity, stability and resistance to corrosion) of designed catalysts regarding its electrochemical surface area, its porosity, its amount of nitrogen and/or cobalt, the size and the repartition of Co NPs etc... This work permits to identify key parameters that have to be considered to further improve non noble-metal catalysts that aim to replace platinum for the ORR.

[1] Z. Chen, D. Higgins, A. Yu, L. Zhang, J. Zhang, Energy & Environmental Science, 4 (2011) 3167-3192.
[2] A. Morozan, B. Jousselme, S. Palacin, Energy & Environmental Science, 4 (2011) 1238-1254.
[3] A. Morozan, P. Jégou, M. Pinault, S. Campidelli, B. Jousselme, S. Palacin, ChemSusChem, 5 (2012) 647-651.
[4] A. Morozan, P. Jegou, B. Jousselme, S. Palacin, Physical Chemistry Chemical Physics, 13 (2011) 21600-21607.
[5] S. Le Vot, B. Jousselme, Publication in preparation.

Numerical analysis of vanadium and water crossover effects in all-vanadium redox flow batteries

Kyeongmin Oh, Seongyeon Won, and Hyunchul Ju
Department of Mechanical Engineering, Inha University
100 Inha-ro, Nam-gu, Incheon 402-751, Republic of Korea
hcju@inha.ac.kr

In this work, a numerical analysis of vanadium ion and water crossover phenomena in vanadium redox flow batteries (VRFBs) is presented during charging and discharging process. The model is further enhanced from our previous 3-D thermal VRFB model [1] with consideration of vanadium ion crossover and water crossover through the membrane. The key physicochemical phenomena including the electrochemical reactions, heat generation, and species transport are well considered in the model, and then applied to a simple VRFB geometry (Fig.1). By using the model, the capacity loss due to the vanadium ion crossover is well illustrated during a single charge/discharge cycle, showing the difference in species distributions owing to the side reaction. In addition, the water crossover through the membrane is investigated along different types of transportation phenomena. According to the paper of C. Sun et al. [2], the transfer of water was classified into four forms depending on driving forces, i.e. concentration difference, charge equilibrium, osmosis, and internal electric circuit formation. These water transport mechanisms through the membrane are implemented in the model and the simulation results show the influence of the vanadium ion and water crossover on the charging/discharging cycle. Furthermore, the detailed contours of vanadium ion and water concentration and overpotential distributions in the positive and negative electrodes are provided to improve an understanding of the vanadium ion and water crossover.

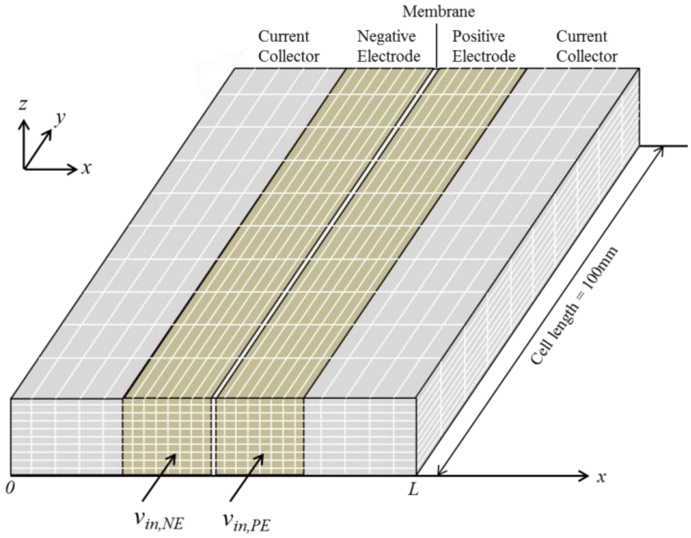


Figure 1. Computational domain and mesh configuration of a simple VRFB geometry.

References

[1] K. Oh, H. Yoo, J. Ko, S. Won, H. Ju, Three-dimensional, transient, nonisothermal model of all-vanadium redox flow batteries, Energy, In press.
[2] C. Sun, J. Chen, H. Zhang, X. Han, Q. Luo, Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery, J. Power Sources 195 (2010) 890-897.

Adenine-Thymine Co-adsorption at Gold Electrodes as a Function of pH: An in-situ FT-IR Spectro-electrochemical Study

Manuela Rueda, Julia Alvarez-Malmagro, Francisco Prieto
Department of Physical Chemistry University of Seville.
c/ Profesor Garcia Gonzalez 1. 41012 Seville. SPAIN
tfn. +34955421015
marueda@us.es

The interactions between complementary DNA bases are important in genetic expression and replication and the adsorption and co-adsorption of these bases on solid substrates have implications in biotechnological applications. These facts have stimulated the study of the structures of adsorbed bases on metal electrodes at a molecular level. In this respect, modern in-situ FTIR techniques that provide chemical specificity and high sensitivity can be combined with electrochemical methods in order to characterise the interactions at electrode interfaces [1].

The co-adsorption of thymine and adenine on gold thin-film electrodes from acid solutions has been previously studied by surface-enhanced infrared absorption spectroscopy in the attenuated total reflection mode (ATR-SEIRAS) [2]. The results suggest a rearrangement of both molecules on the electrode surface in a cooperative process in order to facilitate the Watson–Crick (W–C) and/or Hoogsteen (HG) interactions between the bases, as the atoms involved in these interactions are also the most probably sites of interactions with the metal. However other interactions as π-stacking interactions among the bases must also be considered. On the other hand recent studies about the influence of pH on adenine adsorption on gold electrodes have shown that the two acid-base equilibriums of adenine are modified at the electrode interfaces [3, 4].

In this work the co-adsorption of the complementary DNA bases adenine and thymine on gold thin-film electrodes is studied in a wide pH range (from pH 1 to 12) by ATR-SEIRAS. The experiments have been performed using H_2O and D_2O as solvents. The spectrums of the co-adsorbed bases as a function of potential are analysed and compared to the spectrums of each adsorbed base. Different tautomers of thymine and different acid-base forms of adenine are adsorbed, depending on the pH value. The analysis of the representative vibration modes of the molecules as a function of pH and of potential and their changes upon co-adsorption allow us to decide about the adsorption behaviour of the different forms implied in acid-base and tautomeric equilibriums and the interactions between them.

1.- M. Osawa, in: C. Alkire, D. Kolb, J. Lipkowski, P.N. Ross (Eds.), Diffraction and Spectroscopic Methods in Electrochemistry, vol. 9, Wiley-VCH, Weinheim, 2006, pp. 269–314.
2.- M. Rueda, F.Prieto, J. Alvarez-Malmagro, A. Rodes, *Electrochem. Commun.* 35 (2013) 53.
3.- M. Rueda, F. Prieto, A. Rodes and J.M. Delgado, *Electrochim. Acta*, 82 (2012) 534.
4.- J Alvarez-Malmagro, F. Prieto, M. Rueda, A. Rodes, *Electrochim. Acta*, 140 (2014) 476.

Electrochemical Machining - shaping by anodic dissolution

M. M. Lohrengel[1], K. P. Rataj[2], C. Schnitter[2]
[1]*Institut für Physikalische Chemie und Elektrochemie, Heinrich-Heine-University Duesseldorf,*
Universitaetsstr. 1, D-40225 Duesseldorf, Germany
[2]*H.C. Starck GmbH, Goslar, Germany*

Electrochemical Machining (ECM) is widely used to produce products of high quality from metals and alloys. The work pieces are shaped by controlled anodic dissolution at extremely large current densities of about 100 A/cm^2 in neutral solutions (normally aqueous $NaNO_3$). The advantages of this fast and effective technique are obvious: Almost no tool wear (cathode), almost forceless machining, low roughness without additional process steps, high surface quality and no thermally influenced machining zones. Many high quality parts are prepared by ECM, from shaver heads to turbine blades. An investigation of the fundamental electrochemical process by common electrochemical instruments or even a quantitative product analysis is difficult due to the size of the machines, the extreme absolute currents (several 100 A) and the large electrolyte volumes (some 1000 L) necessary in industry to remove dissolution products at those currents.

Therefore, scaling down of the experimental set-up by some orders of magnitude was necessary. We developed a special flow-through capillary microcell with potentiostatic control in a 3-electrode arrangement [1, 2]. The active area of the working electrode was reduced to 10^{-3} cm² which enabled current densities of some 100 A/cm² at moderate absolute currents around 1 A. Products were quantified at the electrolyte outlet by on-line photometry (metal ions) or fluorescence quenching (oxygen, [3]). This equipment enabled for the first time a quantitative analysis (amounts and valences of all products) under these conditions and led to detailed models of the interface kinetics.

As a result, the surface is described as a layered structure of an oxide film of some nm [4–7], adjacent to the metal surface, and, above a supersaturated, meta-stable viscous product film (some µm) which is continuously removed by electrolyte flow. Most metals or alloys dissolve under these conditions, and, due to their different chemical behavior, fundamental dissolution mechanisms can be classified such as one–step or two-step anion makers (e.g. Mo, Cr, Mn), high-field oxide makers (e.g. Al) or spinel makers (which form oxides of the spinel type Me_3O_4), e.g. Fe, Invar steel or special phases such as Al_3Fe.

Oxygen evolution is on metals such as Fe close to 100% of charge at common current densities around 1 A/cm², but reduces with increasing potential to about 10% of charge at >10 A/cm².

Literature:

[1] MM Lohrengel, A Moehring, M Pilaski, Fresenius J. Anal. Chem. 2000, 367, 334-339
[2] MM Lohrengel, A Moehring, M Pilaski, Electrochim. Acta 2001, 47, 137-141
[3] KP Rataj, C Hammer, B Walther, MM Lohrengel, Electrochim. Acta 2013, 90, 12-16
[4] MM Lohrengel, Mater. Manufact. Proc. 2005, 20, 1-9
[5] C Rosenkranz, MM Lohrengel, JW Schultze, Electrochim. Acta, 2005, 50, 2009-2016
[6] MM Lohrengel, C Rosenkranz, D Rohrbeck, Microchim. Acta 2007, 156, 163-166
[7] B Walther, J Schilm, A Michaelis, MM Lohrengel, Electrochim. Acta 2007, 52, 7732-7737

Mapping Oxygen Reduction at Nanostructured Catalysts: From Ensembles to Individual Particles

Michael A. O'Connell, and Andrew J. Wain
National Physical Laboratory (UK)
Hampton Road, Teddington. TW11 0LW
mike.o-connell@npl.co.uk

Linking the nanoscale behavior of electrochemical interfaces to macroscale performance is vital to developing the next generation of electrochemical devices for energy capture, conversion and storage. Scanning electrochemical microscopy (SECM) and related techniques address this need by combining the wealth of information that can be gained from analytical electrochemistry with the spatial resolution inherent to scanned probe microscopy (SPM). Recent developments in such techniques have sought to reduce the scale of mapping to the single particle level and below, whilst maintaining the broad functionality of the associated probes.

Herein we present our latest advances in tailoring such methods to study the oxygen reduction reaction (ORR) at catalytic nanoparticle decorated surfaces. Our technique of choice is combined scanning electrochemical – scanning ion conductance microscopy (SECM-SICM), which is implemented in a variety of imaging modes to visualize the ORR at electrochemically deposited nanoparticle ensembles. Significantly, mapping at the individual particle level of both competitive oxygen reduction [1] and hydrogen peroxide generation [2] at ensembles of Pt and Au particles respectively, is realized. Complementary macroscale electrochemistry, including under potential deposition and rotating ring-disk voltammetry, provides valuable mechanistic insights into related ensemble behavior.

References

[1] M. A. O'Connell, A. J. Wain, *Analytical Chemistry*, 86 (2014), 12100–12107
[2] M. A. O'Connell, J. R. Lewis, A. J. Wain, *In preparation*

Multi-Scale Modeling of Degradation of Pt-Ru Alloy Particles for Anode Catalyst in PEFC Fuel Cell

Md. Khorshed Alam and Hiromitsu Takaba

Department of Environmental and Energy Chemistry, Kogakuin University
2665-1 Nakano, Hachioji, Tokyo 192-0015, Japan
e-mail:takaba@cc.kogakuin.ac.jp

Low temperature fuel cells function by converting the energy released in the oxidation of hydrogen or other hydrogen containing fuels into electrical energy [1]. If pure hydrogen is used as the fuel, Pt is a good anode material, but Pt anodes are deactivated by little amount of CO in the H_2 fuel [2]. It is well established that the catalytic properties of metal can be markedly changed by alloying with a second metal in polymer electrolyte fuel cells [3]. Pt-Ru alloys are known to substantially improve the catalytic performance in the electrochemical oxidation of CO from CO contaminated hydrogen fuels. Among the binary systems the Pt-Ru combination has proved to be most successful at enhancing electro-catalytic activity [4]. The CO itself is usually assumed to follow a so-called bifunctional mechanism, originally suggested by Watanbe and Motoo [5]. For H_2 oxidation in the presence of CO, Watanabe and Motoo have proposed a combined mechanism, in which the ligand and bifunctional effects may coexist [4,5]. The improvement of the catalytic performance requires an understanding of the reaction mechanism at the atomistic level. Multi-scale simulation study of the electro-oxidation of CO at the Pt-Ru alloy interface is very important to provide new insights into the reaction mechanism.

All calculations were performed using density functional theory (DFT) under the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and Monte Carlo (MC) simulation method. The computational method used in the present study is implemented in the DMol^3 [6]. MC simulation has been performed to know the stability of Pt-Ru alloy catalysts during CO oxidation processes.

Pt-Ru surface is modeled as a five layer slabs with Pt:Ru (2:3) ratio. Initially, we have checked the surface stability of Pt-Ru surface with different positions of Pt and Ru remaining same mixing ratio. We found that fcc based Pt-Ru alloy shows higher stability than the hcp based alloy and we also confirmed that the surface coverage with Pt atoms indicates stable combination. We also notice that 2nd layer positioned with Ru atoms shows higher stability than the other combinations. As a whole the tendency indicates, top surface contains Pt sufficiency and 2nd layer contains Ru sufficiency make the structure stable. Model of Pt-Ru surface where CO are located on the atop, bridge and hollow sites were also examined. We found that the well mixing of Pt by Ru leads to a weaker bond of CO on the surfaces. Many studies assumed that Pt-metal alloy shows more reactivity than pure Pt for CO oxidation but very few studies regarding atomistic level. Coverage change of Pt on the surface of alloy catalysts is further studied by MC simulations. Based on the DFT calculations we correlate the binding energy of alloy catalysts with different Pt coverage. We performed MC simulation in the presence of gases (H_2,CO and H_2O). From our MC simulation study we successfully modeled the temperature effect on Pt-Ru alloy surface change as well as CO poisoning influence to Pt coverage of this bimetallic surface.

References

1. M. Gotz, H.Wendt, *Electrochim. Acta* **43**, 3637(1998).
2. R.A. Lemons, *J. Power Sources* **29**, 251(1990).
3. V. Ponce, G.C. Bond, Catalysis by Metals and Alloys; Studies in Surface Science and Catalysis *95; Elsevier: Amsterdam,* 1995.
4. M.Watanabe, M. Uchida, S. Motoo, *J. Electroanal. Chem.***229,** 395 (1987)
5. M. Watanabe, M. Shibata, S. Motoo, J. *Electroanal. Chem.* **206**, 197 (1986)
6. B. Delley, *J. Chem. Phys.* **92**, 508 (1990)

SECM Writing and Reading with an Original Dual Microelectrode

Vasilica Badets[1], Damien Quinton[1], Olivier Fontaine[2], Dodzi Zigah[1]
[1]*Univ. Bordeaux, ISM, UMR 5255, F-33400 Talence, France*
[2]*Univ. Montpellier 2, UMR 5253, CC1701, 34095 Montpellier France*
kwamidodzi.zigah@u-bordeaux1.fr

Surface patterning with molecules is becoming a reliable tool for a large range of applications such as analytical science or molecular electronic. The development of Scanning Electrochemical Microscopy (SECM) allows to locally modify surfaces using electrochemical reactions generated by a microelectrode. Click chemistry coupled with SECM is a very easy way to locally modify surfaces with a large variety of molecules[1,2,3].

In this work we present an original surface modification using a unique dual copper-gold microelectrode. The copper electrode is used to "write" on the surface meanwhile the gold electrode is used to "read" the modification. The entire surface of glassy carbon was firstly modified by electrografting of an aryldiazonium salt containing an azide moiety. Secondly, the local azide-alkyne cycloaddition using a ferrocene alkyne was performed by a Cu(I) ion generated at the copper electrode. This click reaction was located in a small area under the copper part of the microelectrode positioned closely to the surface. This "writing" reaction was followed by a "reading" procedure in which the ferrocene immobilized on the surface was observed by SECM in feedback mode. For this, the gold part of the dual microelectrode was used. This procedure proves the versatility of systems that could be developed using the newly presented click coupled SECM dual microelectrode setup.

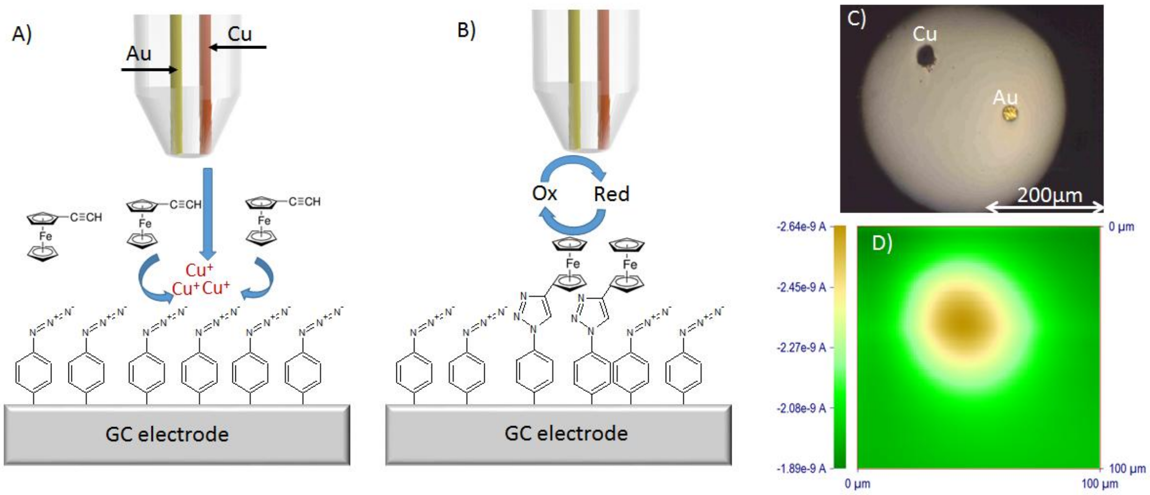


Fig. 1. A) Generation of Cu(I) by oxidation of Cu microelectrode. B) Feedback mode to observe the immobilized ferrocene using the Au microelectrode. C) Optical image of the dual microelectrode. D) SECM image of the immobilized ferrocene in feedback mode.

References

[1] S. Lhenry, Y.R. Leroux, C. Orain, F. Conan, N. Cosquer, N.L. Poul, O. Reinaud, Y.L. Mest, P. Hapiot, Locally Induced and Self-Induced "Electroclick" onto a Self-Assembled Monolayer: Writing and Reading with SECM under Unbiased Conditions, Langmuir 30 (2014) 4501-4508.
[2] D. Quinton, A. Maringa, S. Griveau, T. Nyokong, F. Bedioui, Surface patterning using scanning electrochemical microscopy to locally trigger a "click" chemistry reaction, Electrochem. Commun. 31 (2013) 112-115.
[3] S.-Y. Ku, K.-T. Wong, A.J. Bard, Surface Patterning with Fluorescent Molecules Using Click Chemistry Directed by Scanning Electrochemical Microscopy, J. Am. Chem. Soc. 30 (2008) 2392-2393.

Development and characterization of electrocatalytic layers based on reduced graphene oxide for PEM fuel cell applications

S.A. Grigoriev[1], I.V. Maruseva[2], A.S. Pushkarev[2], V.N. Kalinichenko[3], P. Millet[4], V.N. Fateev[2]
[1] National Research University "Moscow Power Engineering Institute",
Krasnokazarmennaya str., 14, 111250, Moscow, Russia
sergey.grigoriev@outlook.com
[2] National Research Center "Kurchatov Institute",
Kurchatov sq., 1, 123182, Moscow, Russia
[3] DELTARUS Limited,
2/5(B), Likhachevsky alley, Dolgoprudny, Moscow region, 141700, Russia
[4] Institut de Chimie Moléculaire et des Matériaux, UMR CNRS n 8182,
Université Paris Sud 11, 91405 Orsay Cedex France

The use of various nanoforms of carbon as electrocatalyst carriers in PEM-based electrochemical systems is aimed at increasing the activity and stability of electrodes and simultaneously decreasing noble metals contents [1]. In this paper we report on the synthesis and characterization of nanostructured electrocatalytic materials made of reduced graphene oxide (RGO) doped with platinum and non-platinum metals and theirs complexes.

Graphite oxide was synthesized using the modified Hammers's method [2]. Functionalized RGO-based materials were produced by exfoliation of graphite oxide. In addition, the oxidized or fluorinated forms of graphite were modified and subsequently reduced. RGO was impregnated with platinum metallic nanoparticles using chemical method or magnetron-ion sputtering in pulse mode. Non-precious metals inorganic complexes have been deposited onto RGO using experimental techniques from coordination chemistry.

Structural and electrochemical properties of the synthesized electrocatalytic materials have been investigated using TGA, TEM, SEM, XRD, XAFS-spectroscopy (EXAFS+XANES), and cyclic voltammetry.

Results showed that these RGO-based catalytic materials possess high electrocatalytic activity, high electrochemical stability, permeability for reactants and reaction products (in a gas and liquid phase) and high electronic conductivity. In particular, RGO with high conductivity and specific surface area (600 m^2/g) has been synthesized (figure 1). After deposition of Pt nanoparticles (figure 2), electrochemically-active surface area as high as 50 m^2/g were obtained.

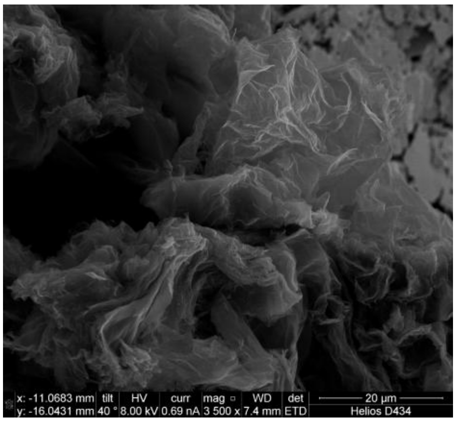


Figure 1. SEM-image of synthesized RGO nanorosettes

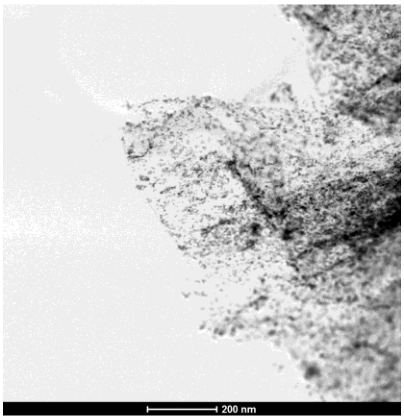


Figure 2. TEM-image of RGO sheet decorated by Pt nanoparticles

Synthesis and characterization of RGO, and RGO impregnated by non-noble metal and complexes was financially supported by the Russian Foundation for Basic Research within the framework of research project No. 14-29-04071 ofi_m. Synthesis of platinum metal nanoparticles on RGO by magnetron-ion sputtering in pulse mode was performed at the expense of a grant of the Russian Scientific Foundation (project No. 14-29-00111).

References

1. Dai L., Chang D.W., Baek J.-B., Lu W. // Carbon Nanomaterials. 2012. V. 8. No 8. P. 1130.
2. Hummers W.S., Offman R.E. // J. Amer. Chem. Soc. 1958. V. 80. P. 1339.

Dual role of hydroxide adsorption for borohydride electrooxidation reaction on Platinum.

Pierre-Yves Olu*, Antoine Bonnefont, Marlène Rouhet, Sébastien Bozdech, Elena Savinova ,
Nathalie Job, Marian Chatenet
[1]*Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France*
[2] *CNRS, LEPMI, F-38000 Grenoble, France*
pierre-yves.olu@grenoble-inp.org

The borohydride electrooxidation is a promising reaction that merits further consideration as an anodic reaction for direct borohydride alkaline fuel cell (DBFC). Amongst other advantages, it displays low thermodynamic potential ($E^0 = -1.24$ V *vs.* NHE), high capacity (5.7 Ah.g^{-1}) and absence of CO poisoning. Nevertheless, a better understanding of the borohydride electrooxidation reaction (BOR) mechanism is needed for future development of the DBFC technology. However, the study of the BOR mechanism is a difficult challenge as this 8-electron overall reaction competes with a non-faradaic heterogeneous hydrolysis reaction and involves several intermediate species that can be adsorbed on the Pt surface or released in solution [1].

This complex reaction is very sensitive to the state of surface of the Pt electrode. Cycling a smooth polycrystalline Pt electrode in alkaline electrolyte within the water stability domain prior to the BOR characterization radically changes the shape of the BOR voltammogram obtained in hydrodynamic conditions using the rotating disk electrode (RDE) setup. These changes are easily observable when compared to the common BOR voltammogram measured on a smooth polycrystalline Pt electrode just polished before the BOR RDE study (see Figure) [2]. We proposed the hydroxide adsorption on the Pt surface to be a main actor in both the catalytic surface deactivation (by blocking the free active Pt sites) and reactivation (by a Langmuir-Hinshelwood type reaction with other BOR adsorbed intermediates) starting from ca. 0.5 V *vs.* RHE on voltammogram of the Figure.

Using an electrode composed of Pt nanoparticles supported on vertically aligned carbon nanotubes (VACNT) [3], we studied a wide range of Pt loading towards the BOR and demonstrated the influence of the number of active Pt site for the BOR. A model for the BOR mechanism was proposed taking into account the dual role of hydroxides adsorption. The simulated voltammograms using this model reproduced the main features of the experimental BOR voltammograms on Pt/VACNT and smooth polycrystalline electrodes, and improved the understanding of the BOR mechanism.

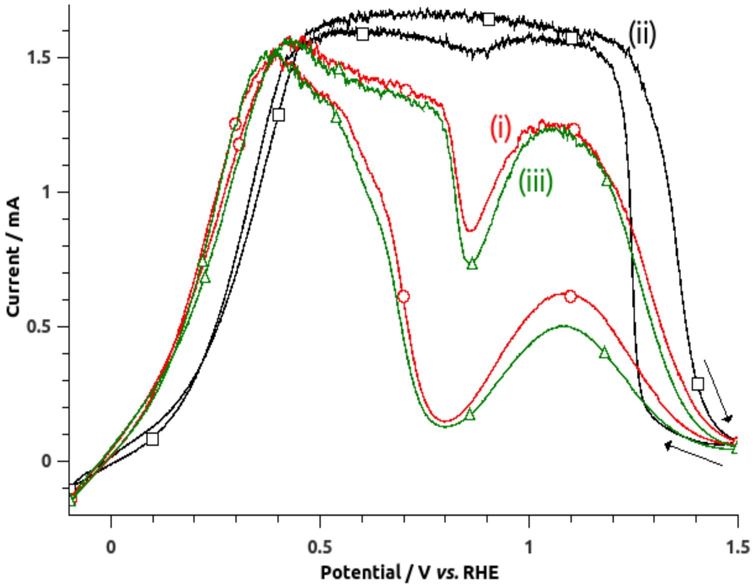


Figure: RDE voltammograms of a Pt disk electrode in 10 mM $NaBH_4$ + 1 M NaOH, $\nu = 25$ mV·s^{-1}, $\Omega = 1000$ rpm. Influence of the electrode preparation procedure:
(i) polishing and ultrasonic cleaning,
(ii) polishing, ultrasonic cleaning and 100 cycles in 1 M NaOH between −0.1 and 1.5 V *vs.* RHE,
(iii) polishing, ultrasonic cleaning, 100 cycles in 1 M NaOH between −0.1 and 1.5 V *vs.* RHE, polishing and ultrasonic cleaning again.

[1] J.P. Elder, A.H. Hickling, Trans. Farad. Soc., 58 (1962) 1852.
[2] P.-Y. Olu, B. Gilles, N. Job, M. Chatenet, Electrochem. Commun., 43 (2014) 47-50.
[3] P. S. Ruvinskiy, et al., Electrochim. Acta, 55 (2010) 3245-3256.

Chemical Structure and Dynamics of Functional Materials for Electrochemical Systems Investigated by Nuclear Magnetic Resonance Spectroscopy

Oc Hee Han
Western Seoul Center, Korea Basic Science Institute
University-Industry Cooperation Building, 150 Bugahyun-ro, Seodaemun-gu, Seoul 120-140, Republic of Korea
ohhan@kbsi.re.kr

Nuclear magnetic resonance (NMR) spectroscopy has been one of the powerful analytical methods to investigate chemical structure and dynamics of various molecules in the liquid state such as organic molecules, small proteins and nucleic acids, and the scope of samples to be investigated by NMR spectroscopy has been widely expanded from rock to elastomer with solid-state NMR spectroscopy. Here we present our investigation results of chemical structures and dynamics of electrochemical materials such as electrode catalysts and polymer electrolyte membranes (PEMs).[1] In addition, water dynamics in PEMs probed by various magnetic resonance techniques,[2] *in situ* NMR detection of electrochemical reactions of direct alcohol fuel cells,[3] and identification and quantification of chemicals in liquid exhausts of direct alcohol fuel cells at different operation conditions[4] will be presented as long as time permits. In the presence of Nafion ionomer, which is a binder and proton conductor added to the slurry of catalysts, ^{195}Pt NMR spectra and relaxation times of Pt catalysts clearly showed the enhanced local density of states at the Fermi levels of the surface platinum in carbon-supported platinum catalysts.[5] This indicates that in the presence of Nafion ionomer Pt catalysts become more active toward oxygen reduction but less active toward fuel oxidation. Effect of post-processing such as hot-pressing and stretching on Nafion polymer electrolyte was studied by measuring residual quadrupole splitting of deuterium NMR spectra of ^2D_2O in swelled Nafion.[6] Molecular motion of polymer electrolyte, as demonstrated with sulfonated poly ether ether ketone, which is a representative polycarbonated PEM was also studied as a function of degree of sulfonation and water contents.[7] The aromatic ring-flip motion was decreased at high degree of sulfonation and increased at higher water contents.

References

1. O. H. Han *Progress in Nuclear Magnetic Resonance Spectroscopy* 72, 1-41 (2013)
2. J. Song, O. H. Han, S. Han *Angewandte Chemie International Edition* in press (2015)
3. O. H. Han et al. *Angewandte Chemie International Edition* 51, 3842-3845 (2012)
4. I. Kim et al. *Angewandte Chemie International Edition* 50, 2270-2274 (2011)
5. K. S. Han et al. *Electrochemistry Communications* 11, 466-468 (2009)
6. S. M. Lee, O. H. Han *Bulletin of the Korean Chemical Society* 34(2), 510-514 (2013)
7. Y. Paik, S. A. Chae, O. H. Han,* S. Y. Hwang, H. Y. Ha *Polymer* 50, 2664-2673 (2009)

Acknowledgement: This work was supported by the National Science & Technology Council grant (DRC-14-3-KBSI) and the KBSI grants (T34419, T35419, & T35443) to O. H. Han.

Monitoring the Reactivity of Individual Ag Nanoparticles by High Resolution Optical Microscopy and Electrochemistry

Frederic Kanoufi,[a] Anisha N. Patel,[a] Ariadna Martinez-Marrades,[b] Christopher Batchelor-McAuley,[c]
Kristina Tschulik,[c] Richard G. Compton,[c] Catherine Combellas,[a] Gilles Tessier[b,d]
[a]ITODYS, CNRS UMR7086, Univ. Paris Diderot, 75013, Paris, France; [b]Institut Langevin, ESPCI ParisTech, UMR7587, Univ. Pierre et Marie Curie, 75005 Paris, France; [c]Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Univ. of Oxford, Oxford OX1 3QZ, United Kingdom; [d]Neurophotonics Laboratory, UMR8250, Univ. Paris Descartes, 75006 Paris, France.
frederic.kanoufi@univ-paris-diderot.fr

Nanoparticles are used as nanocarriers of a chemical tag in fields as diverse as catalysis or nanomedecine (for diagnosis or drug-delivery). If the chemical activity carried by the nanoparticles (on their shell or in their core) is pre-determined by their synthesis, it can vary dramatically depending upon their shape, size, surface facets, their chemical environment… To improve the operational efficiency of nanocarriers it is then necessary to measure their local chemical activity under operation with high resolution.

Recently, promising strategies have been afforded by combining high-resolution microscopies and electrochemical actuation for the imaging of the chemical activity of surfaces. This strategy has been extended to the imaging of single electrochemical events at the level of individual nanoobjects.[1,2] This contribution will illustrate such strategy in examples developed in our laboratories. As depicted in Fig.1, we particularly combine light scattering microscopies with electrochemical activation for the in situ 3D monitoring and quantification of electrochemical dissolution of individual Ag nanoparticles.

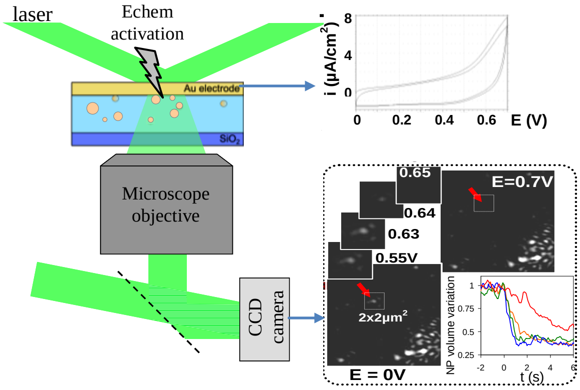


Fig. 1 : Schemactic principle of cyclic voltammetric actuation of colloidal Ag NPs oxidative dissolution monitored individually (red arrow and insert images) in 3D by holography microscopy.

References:
[1] N.J. Tao et al. *Nat. Nanotech.* 7 (2012) 668.
[2] F. Kanoufi et al, *ChemPhysLett* 597 (2014) 20.

Local photoelectrochemical characterization of semi-conducting materials for water splitting

B. Puga,[1] M. Keddam,[1] C. Laberty-Robert,[2] C.M. Sánchez-Sánchez,[1] V. Vivier[1]

1. LISE-CNRS-UMR 8235, UPMC Univ Paris 06, Paris, France
2. LCMCP-CNRS-UMR-7574-Collège de France, Paris, France
vincent.vivier@upmc.fr

Photoelectrochemistry on semiconducting materials is a promising strategy for the conversion of solar energy in a so-called solar fuel cell [1]. This strategy has lead to a large revisiting of water splitting (conversion of water into hydrogen and oxygen), in particular in terms of their material composition [2] and their morphologies [3]. Each electrochemical photoreaction involved in water splitting can be independently studied by means of either a photocathode (for H_2 evolution) or a photoanode (for O_2 evolution) connected to a counter electrode via an external circuit.

A recent strategy consists in investigating arrays of material spots with different nominal compositions, allowing a rapid screening of their photocatalytic reactivity by scanning above the array an optical fiber connected to a Xe lamp as the excitation source [4]. In this work, we extended this strategy in order to measure locally the electrochemical impedance diagrams (Figure 1) of semiconductor materials as a function of the applied potential.

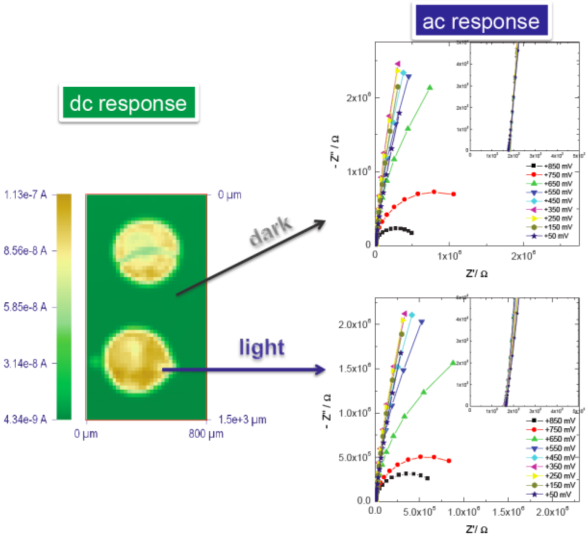


Figure 1:
Electrochemical response of TiO_2 deposits on a glassy carbon substrate obtained by scanning an optical fiber connected to a UV-visible lamp (left), and Nyquist diagrams obtained for different electrochemical potentials when the fiber is above the semi-conductor under illumination od in the dark (right).

In a first step, we will show on a simple model (oxidation of water on TiO_2) how we can perform and interpret such local electrochemical impedance diagrams and how these results compare to conventional EIS obtained on larger samples. Then, preliminary results obtained on array materials of different composition will be discussed.

[1] A.J. Bard, M.A. Fox, Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen, Acc. Chem. Res. 28 (1995) 141-5.

[2] H. Kisch, Semiconductor photocatalysis--mechanistic and synthetic aspects, Angewandte Chemie 52 (2013) 812-47.

[3] Y. Lin, G. Yuan, R. Liu, S. Zhou, S.W. Sheehan, D. Wang, Semiconductor nanostructure-based photoelectrochemical water splitting: A brief review, Chemical Physics Letters 507 (2011) 209-15.

[4] G. Liu, A.J. Bard, Rapid Preparation and Photoelectrochemical Screening of CuInSe2 and CuInMSe2 Arrays by Scanning Electrochemical Microscopy, J. Phys. Chem. C 114 (2010) 17509-13.

Combined AFM-SECM for corrosion studies

C. Kranz[a] J. Izquierdo[b], A. Eifert[a], , R.M. Souto[b]
[b]Institute of Analytical and Bioanalytical Chemistry, University of Ulm
D-89081 Ulm, Germany
[b]Department of Chemistry, University of La Laguna
E-38207 La Laguna, Tenerife, Canary Islands, Spain
Christine.kranz@uni-ulm.de

Electrochemical techniques providing real time localized information play an important role in studying corrosion phenomena. Among those techniques, scanning electrochemical microscopy (SECM) has matured into routine surface analytical technique for corrosion studies [1]. Recently, combined scanning probes techniques such as atomic force microscopy-scanning electrochemical microscopy (AFM-SECM) have been employed in corrosion studies [2,3]. Besides providing high-resolution imaging of topographical changes, the AFM tip-integrated electrode may trigger single pit formation and corrosion products may be monitored. Thus, this technique may contribute to better understanding of involved mechanisms in corrosion. Pitting corrosion at homogeneous substrates reveal a mainly random characteristics of the pitting distribution as pits can only be detected after nucleation. SECM has been used for local modification of the electrolyte composition in close proximity to passive metal surface inducing single pit formation [4,5], where the size of the pits is predominately determined by the size of the microelectrode.

In this contribution, AFM-SECM is used to induce localized single pit formation on passive iron surfaces in a solution containing NaCl and $NaNO_3$. Nitrite ions lead to a passivation of the surface and act as inhibitor of iron corrosion. A break down of the passivation is achieved by the AFM-SECM probe locally generating aggressive species (nitric acid). Pits as small as 1.5 µm in diameter at deliberately chosen locations could be generated, which can be imaged by the AFM tip without requiring the change of probe or solution. In addition, combined AFM-SECM is suitable technique for simultaneously monitoring topographical changes and detecting released species. As an example, the local dissolution of copper during corrosion was monitored. Electrochemical data were obtained in the substrate generation - tip collection mode by reducing the locally generated Cu^{2+} to metallic copper at the AFM tip-integrated electrode, followed by its anodic stripping from the AFM-SECM electrode in bulk solution. As samples electrochemically deposited copper at a platinum microelectrode and a macroscopic copper sample were used and the locally released Cu^{2+} concentration was determined.

References:
[1] R. M. Souto, S. V. Lamaka, S. Gonzalez, Microscopy: Science, Technology, Applications and Education (Eds. A. Méndez-Vilas and J. Díaz, Vol. 3, Formatex, 2010, pp.1769-1780
[2] A. Davoodi, J. Pan, C. Leygraf, and S. Norgren, *Electrochem. Solid-State Lett.* 8 (2005) B21
[3] J. Izquierdo, A. Eifert, R.M. Souto, C. Kranz, Electrochem. Commun. 51 (2015) 15.
[4] K. Eckhard et al., *Electrochem. Commun*. 9 (2007) 1793.
[5] N. Aouina et al., *Electrochim. Acta* 104 (2013) 274.

Implementation of Electrochemical Impedance Spectroscopy (EIS) in symmetric cells for evaluating the post-mortem protocols applied to characterize electrode materials in Li-ion batteries.

Isabel Jiménez Gordon[1], Sylvie Genies[1*], Adrien Boulineau[1], Gregory Si Larbi[1], Mélanie Alias[2] and Viet-Phong Phan[3]
[1]*CEA/Liten (Battery Materials Laboratory), 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*
[2]*CEA/Liten (Electricity Storage Laboratory), French National Institute for Solar Energy, 1130, avenue du Lac Léman, BP 332, 73377 Le Bourget du Lac, France*
[3]*Renault/DE-IR (Advanced Batteries Laboratory), 1 avenue du Golf, 78288 Guyancourt, France*
[*]*Corresponding author: sylvie.genies@cea.fr*

Lithium-ion batteries answer properly to the energy requirements of numerous applications today. Understanding the ageing mechanisms of these systems has become a key issue for the industrial and scientific sectors. Post-mortem analyses are commonly used to assess performance loss causes [1, 2], yet depending on the type of post-mortem test to perform, different *sample preparation protocols* are applied [4, 5]. Herein, Electrochemical Impedance Spectroscopy (EIS) was used to evaluate the reliability of several *sample preparation protocols*, which include different washing and drying conditions. Pouch cells with $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ – polyvinylidene fluoride positive electrode and graphite – carboxymetyl cellulose – styrene rubber negative electrode were opened to recover electrode samples following a given protocol. Then, negative and positive symmetric cells were assembled, and their EIS responses collected. After signal treatment, the EIS of the Pouch cell was reconstructed from the symmetric cells and compared against its real EIS response (figure 1). The impedance results were supported by Transmission Electronic Microscopy (TEM) and Gas Chromatography – Mass Spectrometry (GC-MS) analyses. It was demonstrated that the use of carbonate solvents to remove the salt has a slight impact on the surface properties of both electrodes. Drying at 25° C under the atmosphere of the Ar-filled glove box produces impedance increase, whereas drying at 50° C under vacuum or/and exposition to the dry room atmosphere is very detrimental for both electrodes. Particularly, the positive electrode shows an extra interfacial impedance contribution when drying under vacuum by following a quick evacuation. Independently of the electrode, the more reliable *sample preparation protocol* found consist in washing with a pure linear carbonate solvent and drying under a partial vacuum reached slowly. Not washing the samples is also reliable if the samples are not exposed to the glove box atmosphere for long time. Finally, with the adequate protocol, reconstruction of the Pouch cell EIS signal is possible from symmetric cells. This will allow post-mortem analyses of the EIS response of high energy Li-ion batteries without using reference electrodes.

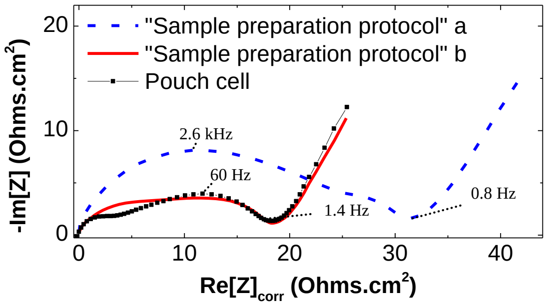


Figure 1. Nyquist plots of the Pouch cell EIS signal at ~4 V, and the respective reconstructed EIS signals from symmetric cells assembled with electrode samples recovered following two different *sample preparation protocols.*

References

[1] T. Waldmann, M. Wilka, M. Kasper, M. Fleischhammer, M. Wohlfahrt-Mehrens, J. Power Sources, 262 (2014) 129-135.

[2] M. Kassem, C. Delacourt, J. Power Sources 235 (2013) 159-171.

[3] J. Woo, V. A. Maroni, G. Liu, J. T. Vaughey, D. J. Gosztola, K. Amine and Z. Zhanga, J. Electrochem. Soc., 161 (2005) A827-A830.

[4] D. P. Abraham, J.L. Knuth, D.W. Dees, I. Bloom, J.P. Christophersen, J. Power Sources, 170 (2007) 465–475.

[5] A. M. Andersson, D. P. Abraham, R. Haasch, S. MacLaren, J. Liu, K. Amine, J. Electrochem. Soc., 149 (2002) A1358-A1369.

New Dimensions in Electrochemiluminescence Sensing

Conor F. Hogan, Paul S. Francis, Gregory Barbante, Egan Doeven, Jacqui Delaney, Sarah Laird.
Dept. of Chemistry and Physics
La Trobe Institute for Molecular Science
La Trobe University, VIC 3083, Melbourne, Australia.
Email: c.hogan@latrobe.edu.au

Electrochemiluminescence provides superior detection sensitivity compared with fluorescence based techniques. However, new materials and new approaches are required before ECL can rival deeply entrenched photoluminescence approaches. We are exploring new avenues of ECL where the emission is influenced by the dimensions of the emitter (quantum dots), the dimension and geometry of the electrode (microelectrodes and transparent micro gap electrodes); as well as experiments where the dimensionality of the data is augmented. For example, we demonstrate the ability to selectively excite luminescent species by modulating the electrochemical potential using a new instrumental approach, combining rapid acquisition of spectral data synchronised with electrochemical experiments. This enables rapid characterization of luminescent redox systems by simultaneous representation on the potential/time and the wavelength axes. This 3D approach to ECL will open up new applications in multiplexed ECL detection heretofore only afforded by traditional photo excitation based techniques. Moreover the ability to continuously vary the emission colour between red and green by scanning the potential of the electrode has important implications for colour selection in light-emitting devices as well as providing fundamental insights into inter-dependent electrochemical and spectroscopic properties and energy transfer mechanisms.

Hierarchical Nanostructured Fuel Cell Electrodes Studied by In-situ Electrochemical Techniques

Cesar A. Barbero,[1] Gabriel A. Planes,[1] Gonzalo García,[2] Elena Pastor,[2]
Angélica Baena Moncada,[1] Rusbel Coneo Rodriguez[1], Paula Cappellari,[1]

1 Chemistry Department, National University of Rio Cuarto, Ruta 8 km 601, 5800-Rio Cuarto, Argentina
2 Departamento de Química Física, Instituto de Materiales y Nanotecnología, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez s/n, 38071 La Laguna, Santa Cruz de Tenerife, Spain
E—mail: cesarbarbero@gmail.com

Fuel cells are the main devices which could be used to convert chemical to electrical energy. However, its development has been hindered by the low efficiency related with the slow kinetics of the electrochemical reactions.

Platinum group metals can be used as electrocatalysts but their scarcity makes them too expensive for massive applications, like electric vehicles. To reduce the amount of metal used, the mechanism of the electrochemical reactions should be understood. Most of the research has been devoted to the reactions at the electrode surface while less attention has been paid to chemical reactions in the solution and mass transport effect. In that way, commercial devices carefully control the chemical composition and morphology of nanostructured catalyst while the actual electrode is fabricated by non-deterministic techniques with little control on the actual morphology of the electrode porosity. Hierarchical nanostructures could be designed to control the mass transport and chemical reactions associated with the electrode reactions.

In the present communication, in-situ electrochemical techniques like Probe Beam Deflection (PBD), [1] Substractively Normalized Fourier Transform Spectroscopy (SNIFTIRS),[2] and Differential Electrochemical Mass Spectroscopy (DEMS),[2] are used to study fuel cell reactions on nanostructured electrodes.

The nanostructuring is made by a variety of methods including hard and soft templating of porous materials, miniemulsion and controlled nucleation synthesis of nanoparticles as well as underpotential deposition of metals.

The target fuel cell reaction is methanol oxidation. However, the oxidation of some intermediates (CO, formic acid) is also studied to gain a better understanding on the effect of electrode morphology on the fuel cell efficiency.

Using the information gathered in the study, fuel cell electrodes with better performance than commercial materials are fabricated.

Acknowledgements

C.A.B and G.A.P are research fellows of CONICET. A.B.M, R.C.R and P.C. thank CONICET for graduate fellowships. The authors wish to thank the EU (IRSES project ‘‘SUMA2-Network’’, Pr. No: 318903) for the financial support for the scientist’s mobility.

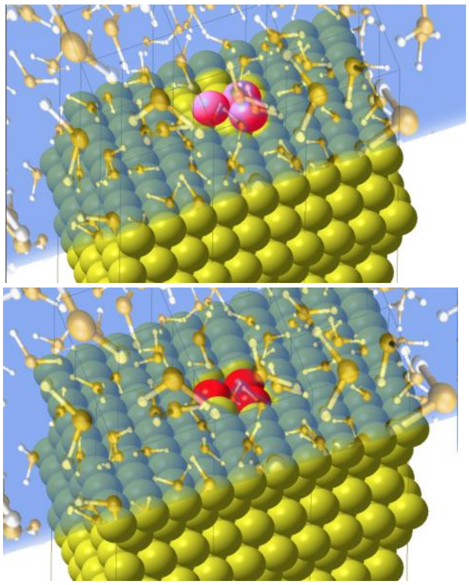
References

[1] Gyözö G. Láng, Cesar A. Barbero, Laser Techniques for the Study of Electrode Processes, Springer, Berlin, 2012

[2] G.A. Planes, E. Moran, J.L. Rodriguez, C. Barbero, Elena Pastor, *Langmuir*, 19(2003)8899–8906

Local reactivity at Pd nanoclusters

Elizabeth Santos[1,2], Paola Quaino[3] and Leandro Moreira de Campos Pinto[4]
[1] *Institute of Theoretucal Chemistry, Ulm Unversity - 89081 Ulm, Germany*
[2] *Instituto de Física Enrique Gaviola, Universidad Nacional de Córdoba, Argentina*
[3] *PRELINE, Fac. Ing. Química, UNL, 3000 Santa Fe, Argentina*
[4] *Lab Eletrocatalise, Faculdade de Ciencias Univ Estadual Paulista, UNESP, Bauru-SP, Brasil*
esantos@uni-ulm.de



Nanostructured surfaces can exhibit surprising chemical, mechanical or electronic properties that are distinctly different from those of extended systems. Especially interesting are their electrocatalytic activity, which can be experimentally obtained by local current measurements with the Scanning Electrochemical Potential Microscopy (SECPM) [1].

In a previous work, we have investigated different Pd nanostructures on Au(111) (monomers, rows, embedded clusters and islands) using our own theory of electrocatalysis [2] and found qualitatively good agreement with experimental data for the hydrogen evolution reaction. Electronic parameters obtained from DFT calculations were introduced in our Hamiltonian and the solvent effects were treated according to Marcus - Hush theory.

However, the modeling of the solvent needs to be improved. Especially when the proton approaches the electrode, the structure of the solvation shell at the transition state, could be very different if the nanostructure is embedded in the surface or not (see Figure). In the case of flat surfaces, the proton should lose a larger number of water molecules in its solvation sheath when it is close to the electrode than in the second case.

We have combined our electrocatalysis theory with molecular dynamic in order to obtain quantitative results. We focus on the Volmer step of the hydrogen evolution reaction and calculate the activation barrier. The potential of mean force (pmf) has been calculated by using molecular dynamics and from this we have derived the energy of solvent reorganization as a function of the distance of the reactant from the reaction site.

References

[1] J. Meier, K.A. Friedrich and U. Stimming, Faraday Discuss. 121, 365 (2002).
[2] P. Quaino, E. Santos, H. Wolfschmidt, M.A. Montero and U. Stimming, Catalysis Today 177 (2011) 55.

Experimental Study of Small Lead Acid Batteries Regeneration Performance Modelling in Time

Astier François[1], Mandin Philippe[1], Boyer Gérémy[2], Merdrignac Odile[3], Noiret Nicolas[4]
[1]LIMatB, Lorient ; [2] BGS, Landivisiau ; [3] Université de Rennes 1, Rennes ; [4] ENSCR, Rennes
[1] Centre de Recherche Christiaan Huygens, Rue de Saint Maudé, 56100 Lorient
[1] philippe.mandin@univ-ubs.fr

Battery ageing and battery performance evolution prediction is one of the energy management key for “a better tomorrow”. The use of lead acid batteries is, nowadays, still increasing despite the poisoned nature of their compounds and despite the use, in constant increasing, of new battery materials and new battery technologies. In deed lead acid batteries are mainly used to start car engine or as primary energy source for forklift or pallet trucks. Another principal application, very spread in Brittany but also present in other part of the country and all around the world, is the storage of electrical energy produces by intermittent energy sources like photovoltaic, wind or tidal powers, which must be stored. Multiple factors influence lead acid batteries ageing depending of the type of batteries technology (vented or opened and VRLAB or sealed) and the kind of use. We focus our experimental study on four of them: the number of ageing cycles (1), the operating current (2), the temperature (3) and the use of electrolyte additives, containing EDTA (4). Factors are investigated on two levels (Table 1).

Table 1: Different levels of investigated factors

Factors levels	Ageing (nb of cycles)	Operating current (A)	Temperature (°C)	additive EDTA (280g/L)
-	5	C/10= 0,4	0	Ø
+	50	C/5= 0,8	25	5 ml/cell

Batteries investigated are 12V, 4Ah 12-YB4L from YUASA. To achieve a controlled batteries ageing, LabVIEW® software was developed. This software allows the monitoring of an electronic load (EA-EL9080-200) for the discharge and a power supply (EA-PSI 8080-60-2U) to perform the charge. We also setup a video test bench for surface electrode direct observation. After wanted ageing cycles achievement, batteries capacities are checked and EIS (Electrochemical Impedance Spectroscopy) is performed on full battery. Then each battery is emptied and the cover is cut and removed. Electrodes are then picked up from battery stack and analyzed in a simplified three electrode set up (CellU): if the negative electrode is analyzed two positive one are used as counter electrodes and the opposite is applied when positive electrode is investigated. This assembling is introduced in colorless container to perform multi-scale analyses. We first do macro analyzes: electrodes and electrolyte conductivity and density measurements. EIS on full cell and half-cell, using Hg/Hg_2SO_4 as reference electrode. Electrode surface behavior direct observation during charge and discharge are also recorded. Then micro-analyses on specific samples are performed, we use MEB/EDX and BET analyzes. To date, half of ageings have been performed and linked analyzes were carried out. We assume to finish experiments this spring and to be able to present finals results during the ISE conference this summer.

In parallel a1D model of lead acid battery was developed based on model made by M. Cugnet in 2009 [1]. We use Comsol Multi-physics® software coupled with Matlab® using the Matlablink® from Comsol. We first set the geometry and coupled physics in Comsol Multi-physics® with suitable limit and initial conditions for one discharge followed by a charge. In order to performed multiple cycles it was necessary to use Matlab to get out final condition from one cycles in Comsol and to set new initial conditions for the next cycle. First results show a good accordance of simulated and experimental data (figure 1).

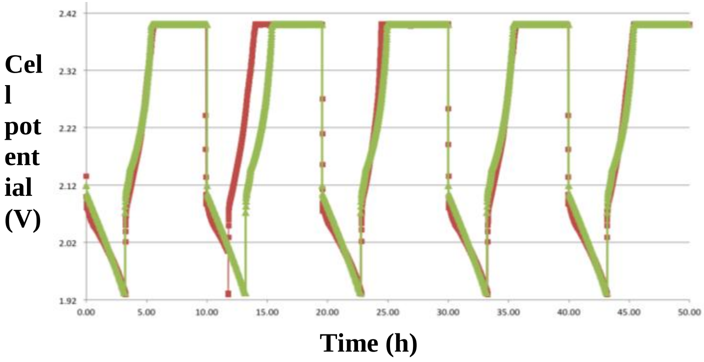
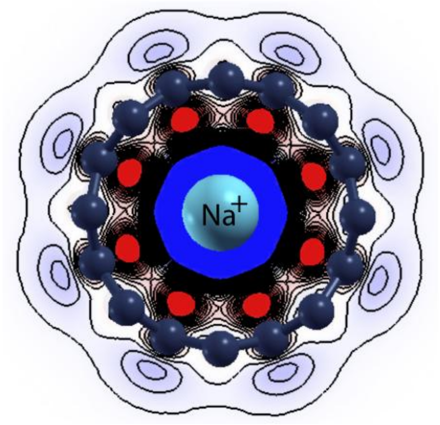


Figure 1: Modeled data (green triangles) in good correlation with experimental data (red squares)

References:
[1] Cugnet & al. *J. Electrochem. Soc.*, **156** (12) A974-A985 (2009)

Ions in Nanopores – Combining DFT with an Effective Hamiltonian Approach

W. Schmickler, L.Mohammadzadeh, A, Goduljan, F. Juarez, P. Quaino, E. Santos
Ulm University
D-89069 Ulm, Germany
Wolfgang.Schmickler@uni-ulm.de



Carbon or metal nanotubes are attractive electrode materials for charge-storage devices. Surprisingly, the capacity per unit area of very narrow nanotubes with diameters less than 1 nm has been found to be greater than that of wider tubes [1]. Kornyshev et al. explained these findings through image effects using classical electrostatics [2]. On the basis of these results they constructed an Ising-like model to calculate the capacity of narrow pores filled with an ionic liquid [3]. In our approach we start from an atomic level and perform DFT calculations for a variety of halide and alkali ions in nanotubes. As electrode material we investigate various types of carbon tubes, both semiconducting and conducting ones, and gold tubes. In narrow tubes, the ions carry unit charge, and their stable position is at the center of the tube [4]. The charge on the ion inside the tube induces image charges in the walls. A typical charge distribution is shown in the figure, which displays a sodium ion in a carbon nanotube (CNT). The positive charge in the center (blue) is balanced by the image charge (red), which sits in front of the carbon atoms. In wider tube, a position near the wall of the tube is more favorable. We discuss the forces which govern the optimum position. Electrostatics and chemisorption favor a position near the wall, while Pauli repulsion favors the center.

In all cases we determined the energy of insertion, which we define as: energy(ion + tube) – energy(tube) – energy (atom). For a given tube diameter, they become more favorable in the order: non-conducting CNT, conducting CNT, gold tubes. We show how the image energy can be obtained on the basis of the screening properties of the tubes, and define an effective image radius for the tubes [5].

In ionic liquids it is quite common that one type of ion is much smaller than the other, and only the smaller ions can enter the nanotubes. On the basis of the DFT calculations described above, we set up a model Hamiltonian for the case of a chain of one type of ion in a long tube. At equilibrium the ions are equidistant, and form a chain of coupled harmonic oscillators:

$$H = N\epsilon(N) + \sum_{j=1}^{N} \omega(N)^2(q_j - q_{j-1}) - \omega(N)^2(q_{j+1} - q_j)$$

Both the energies ε of the ions and the frequency ω depend on the number N of ions in the chain, and are obtained from the DFT calculations; q_j denotes the position of an ion. The statistical mechanics of this simple model can be calculated exactly. In particular, we calculate the electrochemical potential of the ions. The tube is supposed to be in equilibrium with a bulk electrolyte. Changing the electrode potential involves a change in the electrochemical potential, and hence in the number of ions inside the tube. On this basis, we calculate the capacity per area of the tube for a few selected cases.

References

[1] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. Taberna, Science 313 (2006) 1760.
[2] C. Rochester, A. Lee, G. Pruessner, A. Kornyshev, ChemPhysChem 14 (2013) 4121.
[3] A.A.Lee, S. Kondrat, A.A. Kornyshev, *Phys.Rev.Lett.* **113**, #048701, 1-5 (2014).
[4] A.Goduljan, F.Juarez, L.Mohammadzadeh,P.Quaino,E.Santos,W.Schmickler, Electrochem. Comm. 45 (2014) 48.
[5] A.Goduljan, F.Juarez, L.Mohammadzadeh,P.Quaino,E.Santos,W.Schmickler, Electrochim Acta, available online

Influence of Micrometric-Scale Electrode Heterogeneity on Electrochemical Impedance Spectroscopy

Christopher L. Alexander,[1] Mark E. Orazem[1] and Bernard Tribollet[2]

[1]*Department of Chemical Engineering, University of Florida, Gainesville, FL, 32611 USA*
meo@che.ufl.edu
[2]*Laboratoire Interfaces et Systèmes Electrochimiques, CNRS UPR15, Université Paris 6,*
CP 133, 4 place Jussieu, 75252 Paris Cedex 05, FRANCE
bernard.tribollet@upmc.fr

Impedance results showing the influence of time-constant or frequency dispersions are ubiquitous in electrochemistry. Often, these data are modeled by use of a Constant-Phase-Element (CPE). Jorcin et al.[1] have suggested that such CPE behavior can be attributed to surface and/or normal distributions of time constants. This powerful insight has facilitated categorization of different models for extracting meaningful physical properties from CPE parameters. The current best-of-class models are those presented by Brug et al.[2] for surface distributions and the power-law model of Hirschorn et al.[3] for normal distributions.

In early experiments on solid electrodes, micro-scale surface roughness was believed to contribute to the non-ideality of electrochemical measurements. The development of Brug et al.[2] suggests that the CPE behavior could be attributed to a distributed capacity. Pajkossy showed experimentally that annealing can reduce the degree of frequency dispersion even though the roughness of the surface remained the same and thereby concluded that the frequency dispersion cannot be due to the geometric effect alone but may also have a contribution of atomic scale heterogeneities.[4]

This paper describes the results of finite-element simulations used to explore the role of surface roughness, distributed capacitance, and distributed reactivity on the impedance response of a rotating disk and of a recessed disk. The frequency at which roughness or a capacitance distribution influences the impedance response was found in all cases to be higher than the frequency at which the disk geometry-induced current distribution causes a pseudo-CPE behavior.[5] A distribution of reactivity did not cause frequency dispersion.

1. J.-B. Jorcin, M. E. Orazem, N. Pébère, and B. Tribollet, Electrochim. Acta, 51 (2006), 1473-1479.
2. G. J. Brug, A. L. G. van den Eeden, M. Sluyters-Rehbach, and J. H. Sluyters, J. Electroanal. Chem., 176 (1984), 275-295.
3. B. Hirschorn, M. E. Orazem, B. Tribollet, V. Vivier, I. Frateur, and M. Musiani, J. Electrochem. Soc., 157 (2010), C452-C457.
4. T. Pajkossy, Solid State Ionics, 176 (2005), 1997-2003.
5. V. M.-W. Huang, V. Vivier, M. E. Orazem, N. Pébère, and B. Tribollet, J. Electrochem. Soc. 154 (2007), C81-C88.

AFM-LEIS for local electrochemical characterization

Annick Hubin, Thibault Muselle, Diederik Depla, Sara Bals
Vrije Universiteit Brussel (VUB), Research Group of Electrochemical and Surface Engineering
Pleinlaan 2, B-1050 Brussels, Belgium
anhubin@vub.ac.be

Electrochemical Impedance Spectroscopy (EIS) is widely used to obtain global information about samples. For heterogeneous systems, the resulting response of the whole sample's surface is measured. As illustrated in Fig. 1 (left), EIS requires measurement of the voltage across and the current flowing through the system. Either the voltage or the current have to be applied by the set-up.

With the use of an appropriate probe, such measurements can be performed on a smaller scale, obtaining local information about the sample.

When the topography of a system is of interest, Atomic Force Microscopy (AFM) offers valuable information. This also involves a probe to collect data, as illustrated in Fig. 1 (right). Physical interactions between the sample and the sharp extremity of the probe provide topographical information.

Fig. 1: Schematic representation of a global EIS measurement (left) and an AFM measurement (right)

This study shows the combination of AFM with LEIS. This hybrid technique provides simultaneous measurement of impedance and topography on the same area. This assures that both entities represent the same location of the sample at the same moment in time.

Custom modification on thermal AFM probes were performed on the probes used for this set-up. The measurements were performed by incorporating such a modified probe into an electrochemical set-up, as illustrated in Fig. 2.

The local impedance was calculated with the use of local currents instead of global currents (Eq. 1).

$$Z_{global}(\omega) = \frac{U_{global}(\omega)}{I_{global}(\omega)} \qquad Z_{local}(\omega) = \frac{U_{global}(\omega)}{I_{local}(\omega)}$$

Eq. 1: Global impedance (left), local impedance (right)

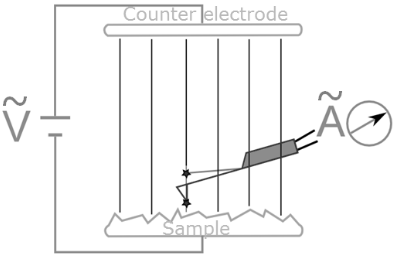


Fig. 2: Schematic representation of a LEIS measurement

Measurements were performed on samples having changes in both topographical and electrochemical properties throughout the surface, to illustrate the ability to determine the local properties of such samples. This provided both topographical and impedance mappings.

Synthesis and Characterization of Novel Pt/$Ti_xM_{1-x}O_2$ Nanocatalysts

Bing Joe Hwang[1,2,*], Chun-Jern Pan[1],Wei Nien Su[3], Mon-Che Tsai[1], Trung-Thanh Nguyen[1], Jyh-Fu Lee[2], Hwo-Shuenn Sheu[2] and Van Thi Thanh Ho[1]

[1]*Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan*
[2]*National Synchrotron Radiation Research Center (NSRRC), Hsinchu 30076, Taiwan*
[3]*Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, Taiwan*
#43, Sec. 4, Keelung Rd., Taipei, Taiwan, 106
bjh@mail.ntust.edu.tw

Fuel cell technology is believed to have the potential to become a major source of clean energy with particularly important applications in transportation. Despite considerable recent advances, existing fuel-cell technology still needs to be improved. Catalyst stability in PEMFC is a critical hurdle and key challenge to their commercialization in stationary and transportation power applications. Currently, fuel cell technology uses carbon black as a catalyst support for both the anodes and cathodes. However, the predominance of weak interactions between the carbon support and the catalytic metal nanoparticles leads to the sintering of the catalytic metal nanoparticles and a consequent decrease in the active surface area with long-term operation. More important, the high potentials that accelerate both electrochemical carbon corrosion and the dissolution of the active elements under normal operating conditions, are issues impacting on fuel cell durability that remain unresolved. This work presents a new approach by exploring robust non-carbon $Ti_xM_{1-x}O_2$ as a novel functionalized co-catalytic support for Pt. This new approach is based on the novel nanostructure of the $Ti_xM_{1-x}O_2$ supports which holds strong metal-support interactions (SMSI) between $Ti_xM_{1-x}O_2$ and Pt that can not only modify surface electronic structure of Pt, evidenced from a shift in the d-band centre of the surface Pt atoms but also provide dual reaction sites for oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR). Furthermore, another benefit of $Ti_xM_{1-x}O_2$ is the extremely high stability of Pt during potential cycling, which is attributable to the SMSI between Pt and $Ti_xM_{1-x}O_2$. Interestingly, $Ti_xM_{1-x}O_2$ can be fabricated as a much thinner catalyst layer, resulting in significantly improved the mass transport kinetics and performance of the resulting membrane-electrode-assembly (MEA).The new approach presented in this work opens a reliable path to the discovery of advanced concepts that may lead to the design of new catalyst materials that can replace the traditional catalytic structures and motivate further research in this field.

A simple approach towards high-performance perovskite-based bifunctional oxygen electrocatalysts

Karina Elumeeva[a], Justus Masa[a], Frank Tietz[b], Wolfgang Schuhmann[a]
[a]*Analytical Chemistry - Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum*
Universitätsstr. 150, D-44780 Bochum, Germany
[b] *Forschungszentrum Jülich GmbH, IEK-1, D-52425 Jülich, Germany*
karina.elumeeva@rub.de

The development of highly active and low cost bifunctional oxygen electrodes is a bottleneck in wide-spread commercialization of renewable energy technologies such as unitized regenerative fuel cells, metal-air batteries and electrolyzers. The main challenge of the design of such electrodes is to achieve high performance and selectivity of both reactions - oxygen evolution (OER) and oxygen reduction (ORR).

A number of approaches have been used to create bifunctional oxygen electrocatalysts including *in situ* formation of systems able to catalyze both reactions [1,2] as well as physical combination of precious metals (like Pt and IrO_2) [3] or non-precious metals (like perovskite and Fe-N doped carbon) [4]. The combination of ORR and OER catalysts into a composite aims producing materials that can retain their individual properties or even slightly alter their activity due to a synergetic effect. However, to date most bifunctional catalyst systems suffer from lack of activity of one reaction leading to wide gap between overpotentials of OER and ORR, low stability or high cost.

Here, we present a simple strategy of modification of oxygen evolving perovskites of general composition $La_{0.58}Sr_{0.4}Fe_xCo_yO_3$ by physical mixing with diverse carbon materials like carbon black, multiwall carbon nanotubes, nitrogen-doped and oxidized carbon nanotubes to incorporate ORR active species. Perovskites of this type were recently found to exhibit activity for OER [5]. By varying the Fe:Co ratio in the perovskite we found out samples with higher performance, that were further modified to obtain bifunctional catalyst systems for both OER and ORR.

The addition of carbon materials to the inks that were further deposited on glassy carbon electrodes sufficiently improve the activity of the formed catalyst layer with respect to the ORR with the best onset potentials and current densities achieved when using nitrogen-doped carbon nanotubes. The improved OER activity is attributed to the improved conductivity in the catalyst film. The difference between potentials measured at current densities of -1 mA cm^{-2} for ORR and 10 mA cm^{-2} for OER in oxygen-saturated 0.1M KOH solution under rotation at 1600 rpm did not exceed 0.85 V, a value which is smaller than for any other bifunctional catalyst obtained from abundant materials.

[1] Zhao A., Masa J., Xia W., Maljusch A., Willinger M-G., Clavel G., Xie K., Schlögl R., Schuhmann W., Muhler M., *J. Am. Chem. Soc.* **136** (2014) 7551-7554.

[2] Tian G.-L., Zhao M.-Q., Yu D., Kong X.-Y., Huang J.-Q., Zhang Q., Wei F., *Small* **10** (2014) 2251–2259.

[3] Zhigang S., BaolianY., Ming H., *J. Power Sources* **79** (1999) 82-85.

[4] Rincón R.A., Masa J., Mehrpour S., Tietz F., Schuhmann W., *Chem. Comm.* **50** (2014) 14760-14762.

[5] Rincón R.A., Ventosa E., Tietz F., Masa J., Seisel S., Kuznetsov V., Schuhmann W., *ChemPhysChem.* **15** (2014) 2810-2816.

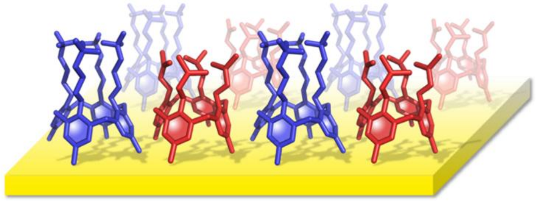
Acknowledgement: Financial support from the Cluster of Excellence RESOLV (EXC 1069) funded by the DFG (Deutsche Forschungsgemeinschaft) and in the framework of Helmholtz-Energie-Allianz "Stationäre elektrochemische Speicher und Wandler" (HA-E-0002) is gratefully acknowledged.

Electrografting at the Molecular Scale

Corinne Lagrost,[a] Luis Santos,[a] Philippe Hapiot,[a] Sébastien Lhenry,[a] Yann Leroux[a], Alice Mattiuzzi,[b]
Ivan Jabin,[b] Nicolas Vandencasteele,[c] Olivia Reinaud[d]
[a]Institut des Sciences Chimiques de Rennes UMR n° 6226, Université de Rennes 1 and CNRS Equipe MaCSE, Campus de Beaulieu, 35042 Rennes cedex, France - [b] Laboratoire de Chimie Organique, Université Libre de Bruxelles (ULB), CP 160/06, 50 avenue F.D. Roosevelt, 1050 Brussels, Belgium – [c]Chimie Analytique et Chimie des Interfaces, Université Libre de Bruxelles (ULB), CP 255, Campus de la Plaine, boulevard du Triomphe, 1050 Brussels, Belgium - [d]Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques UMR n°8601, PRES Sorbonne Paris Cité, Université Paris Descartes and CNRS, 45 rue des Saints-Pères, 75006 Paris, France

corinne.lagrost@univ-rennes1.fr

Surface functionalization is of fundamental importance to design materials with tailored properties or with operating functions. The smooth running, the performance and lifetime of devices that integrate these materials closely depend on the stability of the created interface. For developing applications, chemisorption is then the privileged approach. Thiols self-assembly is a versatile strategy, very easy to process, and allowing the controlled preparation of ultrathin layers (monolayers) on a surface. Using this method, mixed monolayers that permit to finely tune the physico-chemical properties could be readily prepared. But the (electro)grafting of aryldiazonium salts is an alternative strategy that might prove more powerful because i) applicable to a wide range of materials and ii) producing an highly robust interface (covalent binding).[1] However, it is quite tedious to control the formation of monolayers using this approach. Moreover, the reactivity and grafting of the electrogenerated radicals is directed by the reduction potential of the diazonium salts, thus making difficult the surface composition control of mixed monolayers in a one-step strategy.



Herein, an innovative and versatile approach based on the grafting with **calix[4]arene-tetradiazonium salts** is developed and allows the formation of highly robust and densely-packed monolayers on a large range of materials.[2] Homogeneously mixed monolayers could be prepared from a binary mixture of calix[4]arene-tetradiazonium salts in solution.[3] The distribution of the two calixarenes on the surface is directed by their relative molar fraction in the deposition solution as demonstrated by wettability studies, X-ray photoelectron spectroscopy (XPS) analyses and Scanning Electrochemical Microscopy (SECM) The strategy allows the control of the composition of mixed monolayers in a one-step approach. Furthermore, through adequate decoration of the calixarene platform, the introduction of functional molecules or objects (redox molecules, DNA, proteins, nanoparticles…) can be performed with a fine spatial control at the molecular scale. This study contributes to highlight the potential of the diazonium salts electrografting as a competitive alternative to chemisorption strategy like self-assembled monolayers (SAMs) of alkyl thiols in the field of surface functionalization.

---

[1] Pinson, J.; Bélanger, D., ***Chem. Soc. Rev***. **2011**, *40*, 3995-4048

[2] Mattiuzzi, A.; Jabin, I.; Mangeney, C.; Roux, C.; Reinaud, O.; Santos, L. Bergamini, J.-F.; Hapiot, P.; Lagrost, C. ***Nature Commun***. **2012** 3:1130, DOI: 10.1038/ncomms2121

[3] Santos, L.; Mattiuzzi, A.; Jabin, I., Vandencasteele, N.; Reniers, F.; Reinaud, O.; Hapiot, P.; Lhenry, S.; Leroux, Y.; Lagrost, C. ***J. Phys. Chem. C***, **2014**, 118, 15919-15928

Nickel decorated Cu_2O/CuO as a highly efficient photocathode for photoelectrochemical water reduction

Amare Aregahegn Dubale[1], *Chun-Jern Pan*[1], *Andebet Gedamu Tamirat*[1], *Wei-Nien Su*[2,*] *Hung-Ming-Chen*[1],
and Bing-Joe Hwang[1,3*]

[1]NanoElectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan.

[2]NanoElectrochemistry Laboratory, Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan.

[3]National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.

*Corresponding authors: bjh@mail.ntust.edu.tw; wsu@mail.ntust.edu.tw

ABSTRACT:

Here we report the synthesis, design and detail characterization of a novel Cu_2O/CuO hetrojunction decorated with nickel cocatalyst as a highly efficient photocathode for solar hydrogen production. Due to the synergism effect of CuO, the best Cu_2O/CuO hetrojunction yielded remarkably improved photocurrent density (–2.1 mA/cm^2) which is 3.1 times higher than the Cu_2O alone photoelectrode. Meanwhile, a six and twofold further increase in photocurrent density (–4.3 mA/cm^2) has been achieved on the Cu_2O/CuO hetrojunction decorated with nickel cocatalyst compared to that of the Cu_2O alone and the bare Cu_2O/CuO respectively, at 0 V vs RHE under AM 1.5 illumination (100 mW/cm^2). Interestingly, Ni decorated Cu_2O/CuO photocathode revealed an impressive solar conversion efficiency of 2.71% at –0.4 V vs Pt, indicating 467% higher compared with bare Cu_2O/CuO. About 87.7% initial photocurrent density of Cu_2O/CuO decorated with nickel remains after 20 minute of standard solar irradiation at 0 V vs RHE. The increase is more than 1.5 times higher than the bare Cu_2O/CuO (53.6%), suggesting surface modification with Ni not only effectively promotes water splitting but also stabilizes photoelectrode. Faradic efficiency of 84% was obtained for the evolved H_2 gas measurement. The enhanced photoelectrochemical performance attributes to the role of Ni as a protective layer and efficient charge transfer, improved crystallinity and synergism effect of the hetrojunction in light absorption. This inexpensive photocathode with increased photocurrent density and photostability is a highly promising photocathode for solar hydrogen production.

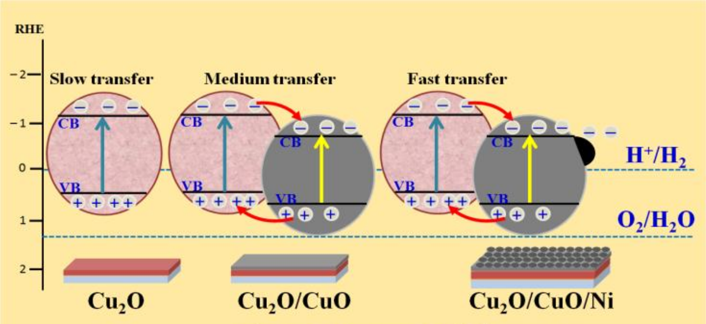


Figure 1 Proposed TOC

KEYWORDS: Photoelectrochemical water splitting, Cu_2O/CuO, hetrojunction, nickel, cocatalyst, photocathode, hydrogen production

Reference:

1. Paracchino, A.; Laporte, V.; Sivula, K.; Grätzel, M.; Thimsen, E. *Nat. Mater.* 2011, 10, 456-461.
2. Dubale, A. A.; Su, W.-N.; Tamirat, A. G.; Pan, C.-J.; Aragaw, B. A.; Chen, H.-M.; Chen, C.-H.; Hwang, B.-J. *J. Mater. Chem. A* 2014, 2, 18383-18397.
3. Tilley, S. D.; Schreier, M.; Azevedo, J.; Stefik, M.; Graetzel, M. *Adv. Funct. Mater.* 2014, 24, 303-311.

Nonlinear behavior of the electron-transfer process

Fabio La Mantia, Andjela Petkovic
Center for Electrochemical Sciences – CES, Ruhr-Universität Bochum
Universitätsstr. 150, D-44780 Bochum, Germany
fabio.lamantia@rub.de

Although the electron-transfer process is considered to be the simplest electrochemical process, its study has been hindered by the capacity to separate the influence of mass transport from the charge transfer. One of the most commonly advanced models used to describe the electron-transfer kinetics is the Marcus theory: the model predicts the correlation between overpotential, η, and current density, i, to have the form

$$i = i_0 \left[\exp\left(\frac{(1-\alpha)RT}{F} \eta \right) - \exp\left(-\frac{\alpha RT}{F} \eta \right) \right]$$

with α linear function of the overpotential. The theory also predicts that α = 0.5 when the electrode potential is equal to the standard potential of the redox couple.

Electrochemical impedance spectroscopy can be used to separate the charge transfer process from the mass transport, however, being a linear technique, it can be used to extract only i_0, but not α. If α is the parameter of interest, several impedance spectra at different ratio of the redox couple can be used to extract it; nonetheless, it is necessary to assume a priori the dependence of α on the potential. In this work, by using intermodulated differential immittance spectroscopy [1], which is a nonlinear technique, it was possible to measure experimentally the value of α at the equilibrium potential under different ratio of the redox couple. It was observed that the value of α is a nonlinear function of the electrode potential, and its value is different than 0.5 at the standard potential condition (see Figure): both observations are in contradiction with the Marcus theory as well as with the Gerischer theory. The results will be discussed in relation to the thermodynamic functions (enthalpy, entropy, and free energy), and to the properties of the interface / electrolyte junction. In particular, the effect of the electric field at the interface on the kinetics of the electron-transfer will be addressed.

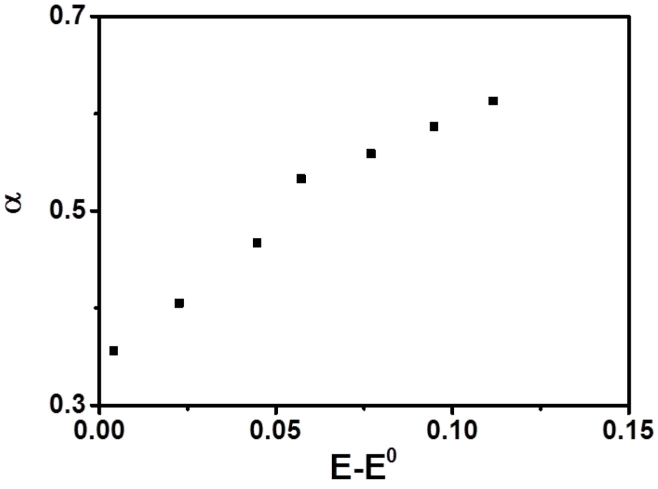


Figure: Value of α at equilibrium conditions as a function of E-E^0. Supporting electrolyte: 0.5M KF; redox couple: ferro-ferricyanide.

[1] A. Battistel and F. La Mantia, “Nonlinear Analysis: The Intermodulated Differential Immittance Spectroscopy,” Anal. Chem., vol. 85, no. 14, pp. 6799–6805, 2013.

Voltammetric and Amperometric Monitoring of Biomarkers Using Non Traditional Electrode Materials and Arrangements

Jiri Barek
[a] *Charles University in Prague, Faculty of Science, Department of Analytical Chemistry,*
UNESCO Laboratory of Environmental Electrochemistry,
Albertov 6, CZ 128 43 Prague 2, Czech Republic
barek@natur.cuni.cz

Monitoring of various biomarkers (of illness, of exposition, of treatment) in various biological liquids is an exciting and challenging task of modern electroanalytical chemistry. It requires extensive search for new electrode materials and arrangements and detailed characterization of these electrodes and investigated systems. Moreover, it requires demanding optimization of potential programs, current responses and composition of measured solutions compatible with determination of various biomarkers in urine and other biological fluids.

This contribution will be devoted to results obtained in our laboratory in the field of monitoring electrooxidizable biomarkers using boron doped diamond film electrodes and microcrystalline-graphite–polystyrene composite film electrode and electroreducible biomarkers using silver solid amalgam electrodes and bismuth film and bismuth bulk electrodes. Both the preparation and pretreatment of these electrodes will be discussed together with their physico-chemical and surface characterization and investigation of electrochemical behavior of tested analytes. Optimization of the newly developed electroanalytical methods based either on batch analysis or analysis in flowing systems will be presented as well together with the description of electrochemical detectors for measurement in flowing systems newly developed for these purposes. New electrode materials and arrangements enabling the transition to single drop measurements and their combination with a preliminary separation and/or preconcentration using capillary techniques will be discussed.

The following model biomarkers and their voltammetric and amperometric determination in body fluids, especially in urine will be discussed:

- 1-Hydroxypyren as an oxidizable biomarker of exposition to polycyclic aromatic hydrocarbons.
- 1-Aminopyren as an oxidizable biomarker of exposition to nitrated polycyclic aromatic hydrocarbons
- Vanylmandelic acid, 4-hydroxy-3-methoxymandelic acid and 4-hydroxy- 3-methoxyphenylacetic acid as an electrooxidizable tumor biomarkers (neuroblastoma)
- Lomustine as an electroreducible biomarker of cancer treatment
- Flutamide and its metabolite 4-nitro-3-trifluoromethylaniline as electroreducible biomarkers of prostatic cancer treatment.

The above discussed methods will be compared with methods based on traditional electrode materials and advantages and disadvantages of both approaches will be summarized.

Acknowledgment

This work was financially supported by the Grant Agency of the Czech Republic (project P206/12/G151).

Effect of Pressure on Titanium Dioxide Electrodeposited Cathodically with Supercritical Carbon Dioxide

Tso-Fu Mark Chang[1,2,*], Wei-Hao Lin[3], Yung-Jung Hsu[2], Chun-Yi Chen[1,2], Tatsuo Sato[1], Masato Sone[1,2]
[1]*Precision and Intelligence Laboratory, Tokyo Institute of Technology*
4259-R2-35 Nagatsuta-cho Midori-ku Yokohama 226-8503 Japan
[2]*CREST, Japan Science and Technology Agency,*
4259-R2-35 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[3]*Department of Materials Science and Engineering, National Chiao Tung University*
1001 University Road Hsinchu Taiwan 30010 Republic of China
[*]*chang.m.aa@m.titech.ac.jp*

Supercritical fluid is any substance at a temperature and pressure above its critical point. Surface tension of supercritical fluid is extremely low and the physical properties can be easily adjusted by pressure and temperature. Therefore, supercritical CO_2 (sc-CO_2) is applied in electrodeposition of materials to overcome problems encountered in continuous miniaturization of electronic components. However, CO_2 is non-polar and has very low electrical conductivity. Thus, a surfactant is used to form emulsions composed of an aqueous electrolyte, sc-CO_2, and the surfactant [1].

Materials electrodeposited with sc-CO_2 emulsified electrolyte (SCE) are reported to have properties very different from that electrodeposited under conventional conditions. Grain refinement and surface smoothening are reported for Ni and Cu films electrodeposited with SCE [1-3]. Grain size of the Ni electrodeposited with SCE could be less than 10 nm [2]. Most interestingly, single crystal or twin crystal structure of Cu are observed when SCE is applied in filling of Cu into the nano-holes [3].

When the SCE is applied in cathodic deposition of TiO_2 films, deposited TiO_2 films are porous, and the films are composed of primary particles and aggregates of the primary particles [4]. Grain coarsening and increase in size of the primary particles are observed for TiO_2 electrodeposited with SCE when compared with the conventional case. ZnO mesocrystals are obtained when SCE is applied in cathodic deposition of ZnO, [5].

TiO_2 obtained from cathodic deposition is usually amorphous. Therefore, an additional heat treatment process, such as 400ºC for 1 hr, is required to have crystalline TiO_2. This heat treatment process would increase the process time, and it could affect properties of the substrate and morphology of the TiO_2 films. In a recently study on cathodic deposition of TiO_2 films with SCE, we found that crystallinity of the TiO_2 could be significantly improved with increase of pressure from atmospheric pressure to 35 MPa. Anatase TiO_2 was obtained at a pressure higher than 25 MPa without any additional heat treatment process. The effect of pressure on crystallinity of TiO_2 deposited is named hydrobaric effect, because the deposition only takes place in the aqueous phase in the emulsions and the effect is similar to the hydrothermal effect in some degree. This is the first report on hydrobaric effect, which is the effect of pressure on chemical reaction conducted in an aqueous solution. We believe the hydrobaric effect can be applied to remove or reduce high-temperature needed in some chemical processes.

Reference:
[1] T.F.M. Chang, M. Sone, A. Shibata, C. Ishiyama and Y. Higo, *Electrochim. Acta*, **55** (2010) 6469.
[2] T. Nagoshi, T.F.M. Chang, S. Tatuo, M. Sone, *Microelectron. Eng*., **110** (2013) 270.
[3] N. Shinoda, T. Shimizu, T.F.M. Chang, A. Shibata, M. Sone, *Thin Solid Films*, **529** (2013) 29.
[4] T.F.M. Chang, W.H. Lin, Y.J. Hsu, C.Y. Chen, T.Sato, M. Sone, *Electrochem. Commun.*, **33** (2013) 68.
[5] W.H. Lin, T.F.M. Chang, Y.H. Lu, T. Sato, M. Sone, K.H. Wei, Y.J. Hsu *J. Phys. Chem. C*, **117** (2013) 25596.

Evaluation of the oxygen reduction reaction activity of nano-oxynitride catalysts with conventional electrochemical techniques

Mitsuharu Chisaka[a], Hirohito Sasaki[a], Noriaki Itagaki[a], Hirokazu Muramoto[b]
[a]*Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan*
[b]*Toyohashi University of Technology, 1-1 Hibarigaoka, Toyohashi, Aichi 441-8580, Japan*
chisaka@eit.hirosaki-u.ac.jp

Success for the development of economic fuel cell-powered passenger vehicles have been considered unclear [1]. Although they have been commercially available using polymer electrolyte fuel cells (PEFCs) in Japanese market since 2014, the high cost and scarce resource of platinum-group-metal (PGM) catalysts used in the catalyst layers could be the barrier for the widespread use. Because the cathodes need one-order larger PGM loading than the corresponding anodes owing to the slow kinetics of the oxygen reduction reaction (ORR) [2], non-PGM ORR catalysts are of particular interests.

Improvement of activity as well as durability are two critical requirements for non-PGM catalysts to be used in vehicles whereas most of the works have focused on the former, activity. Oxide/oxynitride catalysts containing group 4 or 5 metals are promising candidates for PEFC cathodes from the viewpoint of the latter, durability as they are insoluble in the acidic PEFC environment [3,4]. Because this catalyst type is nearly insulator, a conductive support material such as carbon black [5] and reduced graphene oxide [6] is necessary for evaluating their ORR activity. Nonetheless, electron transport could be restricted to the area of the oxide/oxynitride catalysts in contact with the supports as illustrated in Fig. 1 (a). Therefore the evaluation of the activity from all the catalyst surface remained difficult. For providing sufficient conductivity to all the oxide/oxynitride catalyst's surface, we added various carbon sources to the previously reported hydrothermal route [5] to coat conductive layers on the surface of oxynitrides as illustrated in Fig. 1 (b). Then the activity was evaluated with an inexpensive conventional rotating disk electrode method. Effect of the source of carbon, mass ratio of the carbon source to oxynitrides on the measured activity were systematically investigated. Urea powders successfully acted as both nitrogen-dopant and conductive carbon source for enhancing and evaluating ORR activity.

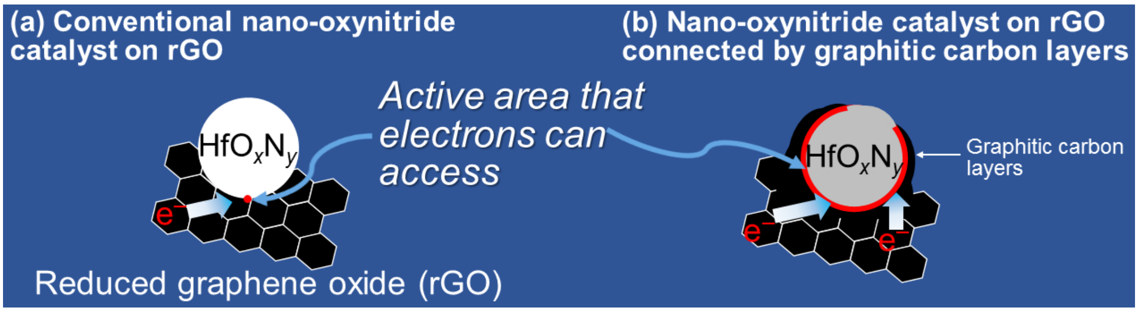


Fig. 1 Schematic image of (a) conventional oxynitride-nanoparticle catalyst supported on reduced graphene oxide sheets and (b) that connected by graphitic carbon layers.

Acknowledgments
This work was partially supported by the Adaptable and Seamless Technology Transfer Program through Target-driven R&D, AS242Z00224L, from Japan Science and Technology agency.

Reference

[1] N. Demirdöven, J. Deutch, Science, 305 (2004) 974.
[2] H. A. Gasteiger, J. E. Panels, S. G. Yan, J. Power Sources, 127 (2004) 162.
[3] A. Ishihara, Y. Ohgi, K. Matsuzawa, S. Mitsushima, K. Ota, 55 (2010) 8005.
[4] M. Chisaka, T. Iijima, T. Yaguchi, Y. Sakurai, Electrochim. Acta, 56 (2011) 4581.
[5] M. Chisaka, Y. Suzuki, T. Iijima, Y. Sakurai, J. Phys. Chem. C, 115 (2011) 20610.
[6] M. Chisaka, H. Sasaki, H. Muramoto, Phys. Chem. Chem. Phys., 16 (2014) 20415.

Combined EDL and transport modeling in water desalination

J.E. Dykstra, A. van der Wal, P.M. Biesheuvel
Wetsus, European Centre of Excellence for Sustainable Water Technology
Oostergoweg 9, 8911 MA Leeuwarden, The Netherlands
Sub-department of Environmental Technology, Wageningen University
Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands
Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands
Jouke.Dykstra@wetsus.nl

Capacitive deionization (CDI) is a novel electrochemical method for water desalination employing porous carbon electrodes [1]. Upon applying a charging voltage, cations are adsorbed in the cathode and anions in the anode, resulting in the desalination of the inflow water, see Fig 1. After the electrodes are saturated, the electrodes can be short-circuited and the ions are released.

During the adsorption phase, ions are transported from the spacer channel, through which the water flows, into the porous carbon electrodes. In these porous carbon electrodes, we distinguish two different types of pores. Firstly, the micropores, where Electrical Double Layers (EDLs) are formed and consequently ions are stored near the charged carbon interfaces. Secondly, we model the macropores, through which the salt is transported to the micropores, subject to diffusional and migrational forces.

The micropores have a pore size of the order of 2 nm or less. For an NaCl solution of 10 mM, the Debye length is approximately 3 nm at 20 ºC, which means that the EDL thickness is about 6-10 nm. As the pore size is smaller than the EDL thickness, EDLs are strongly overlapping and the commonly used Gouy-Chapman-Stern theory to describe these EDLs is not valid. Therefore, we make use of another theory, the improved modified Donnan model, which has shown to describe the salt adsorption in porous carbon electrodes very well for CDI [1,2,3].

To compute the salt adsorption in the electrodes dynamically, we model the transport of salt through the macropores. This transport typically occurs on a length scale of 100s of micrometers. Combining transport and EDL formation in one theory implies combining processes on two vastly different length scales. A second complication in modeling is that the local adsorption of salt from the macropores into the EDLs is infinitely fast, compared to the transport of the salt across the electrode, which requires methods to couple the equilibrium improved modified Donnan model to a dynamic transport model.

To model the dynamic transport and adsorption of salt in CDI systems, we show how we can couple the equilibrium improved modified Donnan model with the dynamic transport model, and we show that we can successfully describe the effluent concentration of a labscale CDI cell as function of time, cell voltage and inflow salinity [1,2,3].

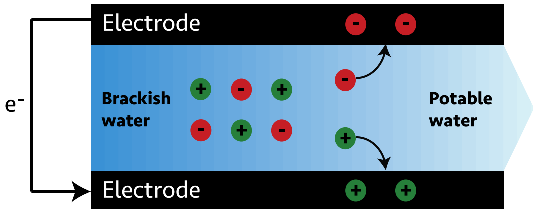


Fig. 1. Salt adsorption in a CDI system

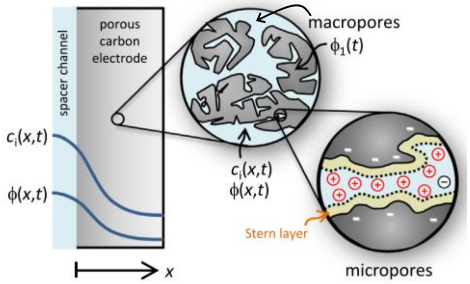


Fig. 2. Modeling transport of salt through macropores and adsorption in the micropores.

References

[1] P. M. Biesheuvel, S. Porada, M. D. Levi, and M. Z. Bazant, J. Solid State Electrochemistry 18 1365-1376 (2014)

[2] T. Kim, J. E. Dykstra, S. Porada, A. van der Wal, J. Yoon, and P.M. Biesheuvel, J. Colloid Interface Sci. (2015), doi: 10.1016/j.jcis.2014.08.041

[2] J. E. Dykstra, P. M. Biesheuvel, A. van der Wal. “Resistance identification and rational design of a Capacitive Deionization process” (submitted, 2015)

Structural, thermal and electrochemical study of single step synthesized WC nanopowder

Gourav Singla, K.Singh and O. P. Pandey
Functional Materials Lab, School of Physics and Materials Science,
Thapar University, Patiala, Punjab, India (147004)
gsinghla@gmail.com

Among transition metal carbides, tungsten carbide (WC) with a wide range of particle size is used for industrial applications. It is a significant challenge to obtain tungsten carbide (WC) nano powder by single step with the existing methods. Here we report simple method to get carbon encapsulated tungsten carbide nanocomposite by single step *in-situ* reduction-carbonization process by reaction between WO_3, Mg and C_6H_{14} in a self-designed autoclave. The samples were characterized by XRD, TEM and HRTEM. The XRD results confirm the formation of tungsten carbide with free carbon in the form of graphite (Figure 1). TEM and HRTEM results show the morphology as well as particle size with the graphite carbon layers outside the tungsten carbide particles. The cyclic voltammetry results show the electrocatalytic activity of synthesized samples.

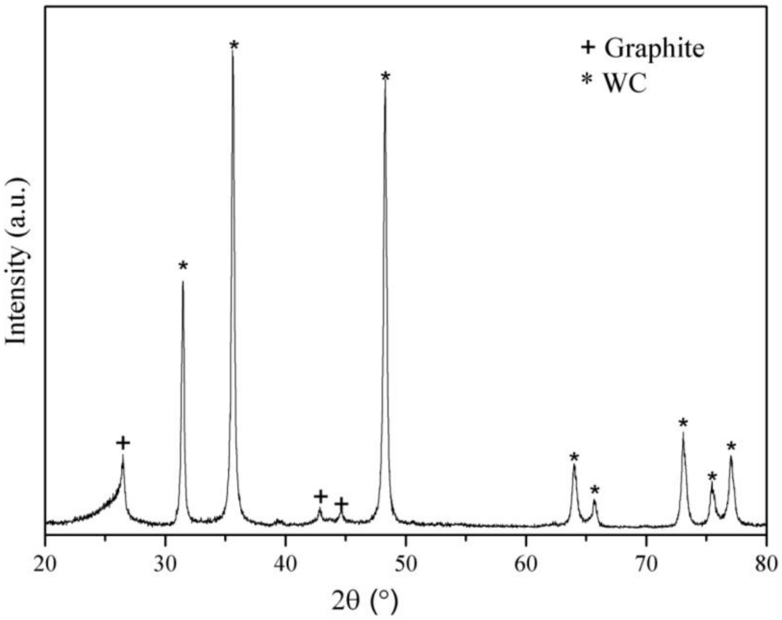


Figure 1. XRD pattern of synthesized carbon encapsulated WC nanopowder.

Possibilities and Limitations of Scanning Electrochemical Microscopy for the Investigation of Corrosion Mechanisms

R.M. Souto, J. Izquierdo
Department of Chemistry, University of La Laguna, P.O. Box 456, E-38200 La Laguna (Tenerife, Canary Islands), Spain
rsouto@ull.es

During corrosion reactions, either well-defined or randomly distributed asymmetries may appear on the surface, leading to the formation of anodic and cathodic regions of typical sizes within the micrometer range or below. As a result, corrosion processes occur at the micrometer or sub-micrometer range, so the involved mechanisms should be investigated employing appropriate methods and techniques. Those techniques must then provide highly localized information in real time and in the *in situ* corrosion conditions. This has motivated the development of several electrochemical microscopies that have contributed to a better understanding of the electrochemical processes occurring on materials undergoing corrosion [1]. Among them, the Scanning Electrochemical Microscopy (SECM) has proved to be a highly sensitive tool for the analysis of diverse types of surfaces and interfaces **[**2**]**. It makes use of an ultramicroelectrode (UME) for the electrochemical analysis of the electrolyte placed in the diffusion layer of a solid - liquid interface. Its spatial resolution is limited by the usual micrometer dimensions of the active microdisks in the UME, typically within 10 to 25 µm in diameter. This spatial range has demonstrated to be enough for the SECM to be effectively employed for the resolution of several corrosion problems [3,4].

One of the major limitations encountered in conventional amperometric operation modes during corrosion research appears when analysing recorded data that are influenced by more than one function. That is, the electrochemical response recorded at the tip may originate from the electrochemical conversion of more than one redox species, from chemical changes in the electrolyte, and from topographic variations of the substrate. On the one side, the evolution of the chemical activity of the surface directly alters the concentration of any electroactive species in the close electrolyte as well as the substrate ability towards electron transfer with those species. On the other side, topographic changes simultaneously occurring due to the local dissolution and passivation phenomena on the metal surface may also affect the tip response by hindering or facilitating the diffusion of the electroactive species towards the probe. In order to distinguish the different contribution affecting the SECM response, other probes than conventional microdisk electrodes were investigated.

This contribution will focus on new developments towards multifunctional imaging in SECM for the investigation of corrosion reactions. The applicability of combinations of various operation modes in SECM, as well as the combination of SECM with other scanning probes techniques, will be illustrated using relevant examples.

References:

[1] P. Marcus, F. Mansfeld (Eds.), Analytical Methods in Corrosion Science and Engineering, CRC Press, Boca Raton, FL, 2006.
[2] A.J. Bard, M.V. Mirkin (Eds.), Scanning Electrochemical Microscopy, 2nd edn., CRC Press, Boca Raton, FL, 2012.
[3] L. Niu, Y. Yin, W. Guo, M. Lu, R. Qin, S. Chen, Application of scanning electrochemical microscope in the study of corrosion of metals, Journal of Materials Science 44 (2009) 4511–4521.
[4] M.B. Jensen, D.E. Tallman, Application of SECM to corrosion studies. In: Electroanalytical Chemistry: A Series of Advances, Vol. 24 (Edited by A.J. Bard, C. Zoski). CRC Press, Boca Raton, FL, 2012, pp. 171-286.

Influence of a passive layer on the kinetics of an electron transfer reaction.

Marie Benoit[1], Christian Bataillon[2], Benoît Gwinner[1] ; Frédéric Miserque[2], Carlos Sanchez-Sanchez[3], Bernard Tribollet[3], Vincent Vivier[3]

[1]*CEA, DEN, DANS, DPC, SCCME, Laboratoire d'Etude de la Corrosion Non Aqueuse, F-91191 Gif-sur-Yvette, France.*
marie.benoit@cea.fr
[2]*CEA, DEN, DANS, DPC, SCCME, Laboratoire d'Etude de la Corrosion Aqueuse, F-91191 Gif-sur-Yvette, France.*
[3]*CNRS - UPMC, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques, F-75252 Paris 05, France.*
vincent.vivier@upmc.fr

In France, the spent nuclear fuel reprocessing involves the use of nitric acid at various concentrations and temperatures up to the boiling point. The corrosiveness of these nitric mixtures leads to the use of corrosion resistant materials such as zirconium or austenitic stainless steels. Indeed, these materials are protected by a passive layer which slows down redox reactions at the metal / nitric acid interface. The objective of this work is to study the role of the passive layer on the kinetics of reduction of nitric acid. As the reduction of nitric acid is very complex in concentrated solution [1-2], we firstly focused on a single step in the reduction reaction (Fe (III) / Fe (II) couple in acidic solution) on passivated zirconium with different oxide layer thicknesses.

A necessary prerequisite was the establishment of a protocol for the growth of the passive layers with a controlled thickness. This was achieved by anodic polarization with monitoring of the thickness by electrochemical impedance spectroscopy (*in situ*) and XPS (*ex situ*). A critical analysis of the results obtained with these two different techniques was done. Two methods of exploitation of the electrochemical impedance spectra were used and discussed: the power law and Jonscher's approaches [3-6]. For XPS analyses, the way to estimate the values of the photoelectrons mean free paths (physical parameters required for estimating the oxide thickness) was shown to be a relevant parameter for both zirconium and zirconium oxide and was thoroughly discussed [7-9]. Finally, it will be shown that both methods are in accordance for passive films with thicknesses up to 8 nm.

The kinetics of the Fe(III) reduction was investigated by different techniques: cyclic voltammetry [10], electrochemical impedance spectroscopy, and scanning electrochemical microscopy [11]. The values of the rate constants k^0 of Fe(III) reduction estimated by these three methods were in good agreement and it was shown that the rate constant k^0 value decreases when the oxide thickness increases. In addition to the kinetics properties, the electrochemical impedance spectroscopy can lead to estimate the semiconducting properties of the film: the space charge capacitance (from the Mott-Schottky equation) allowed to estimate the number of charge carriers in the oxide. These values were shown to follow the same trend than k^0 when the oxide thickness increases.

In a second step, this study performed on the Fe(III)/Fe(II) couple was then extended to the reduction of nitric acid, for which the preliminary results will also be presented.

[1] V.P. Razygraev, et al., Features of cathode reduction of boiling solutions of nitric acid on a platinum electrode, Zh. Prikl. Khim., 61, 1988, p. 71-79.

[2] D. Sicsic in Modélisation thermodynamique et cinétique de la réduction de l'acide nitrique concentré, Université de Pierre et Marie Curie, Paris, 2011.

[3] B. Hirschorn et al., Determination of effective capacitance and film thickness from constant-phase-element parameters, Electrochimica Acta, 55(21), 2010, p. 6218-6227.

[4] D. Sicsic, F. Balbaud-Célérier and B. Tribollet, *Modelling of the nitric acid reduction process: application to materials behavior in reprocessing plants*, Proceedings of ICAPP '12 Chicago, USA

[5] Jonscher, A.K., *A many-body universal approach to dielectric relaxation in solids.* Physics of Dielectric Solids, 1980. Conference on Physics of Dielectric Solids, 1980: p. 22-45.

[6] Bataillon, C. and S. Brunet, *Electrochemical impedance spectroscopy on oxide-films formed on zircaloy-4 in high temperature water.* Electrochimica Acta, 1994. **39**(3): p. 455-465.

[7] M.P. Seah and Dench Surf. Interface Anal. 1 (1979) 2.

[8] S. Tanuma, C.J. Powell, D.R. Penn, Surf. Interface Anal. 21 (1994) 165.

[9] W.H Gries, Surf. Interface Anal. 24 (1996) 38.

[10] Bard, A.J., *Electrochimie : principes, méthodes et applications.* Masson ed1983.

[11] Sidane, D. et al., Electrochemistry Communications, 2011. 13, p.1361-1364.

Ta nanoparticles for electrolytic capacitors

M. Manko[1], M. M. Lohrengel[1], K. P. Rataj[2], C. Schnitter[2]
[1]*Institut für Physikalische Chemie und Elektrochemie, Heinrich-Heine-University Duesseldorf,*
Universitaetsstr. 1, D-40225 Duesseldorf, Germany
Manuel.Lohrengel@uni-duesseldorf.de
[2]*H.C. Starck GmbH, Im Schleeke 78-91, D-38642 Goslar, Germany*

The technical parameters of electrolytic capacitors are mainly determined by their active surface area and by thickness and permittivity of the oxide film, which acts as dielectric medium. In these terms, sintered Ta particles of less than 1 µm are a perfect substrate. They have large surface areas with open pores, withstand mechanical and chemical attacks, and can be easily anodized. A detailed understanding of the oxide layers on sintered electrodes is vital for fabrication, characterization and quality control. This concerns the oxide growth mechanism, the determination of active surface area, the knowledge of oxide thickness before and after anodization, the influence of temperature and particle sizes, the determination of capacitance and identification of side reactions such as oxygen evolution or corrosion (i.e. chemical dissolution of the oxide at the interface oxide/electrolyte).

The oxide growth on macroscopic planar Ta electrodes or wires is well understood in terms of thickness and homogeneity of native and final oxide layers and capacitance. These data, however, does not fit to sintered spherical nano particles with diameters in the 100 nm range [**1**]. Moreover, the small electrolyte volume of the pores means higher resistances, local pH shifts due to hindered diffusion and corresponding shift of equilibrium potentials during anodization. Therefore, differences to macroscopic experiments were expected and investigated in especially modified electrochemical micro cells by cyclic voltammetry, potentiostatic transient methods and impedance spectroscopy.

This concerned the shape of cyclovoltammograms which showed a non-constant plateau current. Finite element simulations of the spherical oxide growth showed similar results but only for smaller particles <50 nm. Finally the effect could be explained by the special sinter structure, in fact the complete oxidation of contact areas (bottle neck effects). Moreover, oxygen evolution, which requires an electronic conductivity of the oxide, was excluded in the former literature and, accordingly, current efficiencies > 99% for anodic oxide formation were reported. In contrast to this, large amounts of oxygen gas are evolved during the anodization of tantalum anodes for electrolytic capacitor fabrication. Bubble formation at macro electrodes, however, is only observed, if the anodic current density exceeds 1 mA/cm², otherwise the oxygen is dissolved in the electrolyte, removed by diffusion and not respected. In sintered bodies, due to their large inner surface of hundreds of cm², supersaturation takes place and bubbles are formed. A quantitative analysis in a special micro set-up [**2, 3**] showed that oxygen is only produced in parallel to significant oxide growth, that only 4% of the total anodic charge are consumed for oxygen and that oxide growth is not affected.

---

1 H. Haas, C. Hammer, M. M. Lohrengel, K. P. Rataj, C. Schnitter, M. Stenzel, CARTS International 2012, Proceedings, Las Vegas, NV, p. 274-285,

2 C. Hammer, B. Walther, H. Karabulut, M. M. Lohrengel, J. Solid State Electrochem. 15 (2011), 1885-1891

3 K. P. Rataj, C. Hammer, B. Walther, M. M. Lohrengel, Electrochim Acta 90 (2013) 12-16

“High Voltage” Li-ion Batteries Electrolyte Formulation for Stable Interfaces

Christopher CHARTON[a, c] ; Jésus SANTOS PEÑA[b, c] ; Agnès BILLER[a, c] ; Matthieu LE DIGABEL[a, c] ;
Daniel LEMORDANT[b, c] ; Hervé GALIANO[a, c]

a. CEA/DAM, Le Ripault – 37260 MONTS, France ; firstname.name@cea.fr
b. Université François Rabelais de Tours, Faculté des Sciences et Technique, PCM2E, parc de Grandmont, 37200 Tours, France ; firstname.name@univ-tours.fr
c. Laboratoire de Recherche Correspondant, LRC CEA/PCM2E, France

Nowadays most used electrolytes are based on mixtures of alkylcarbonates containing $LiPF_6$ as salt. However the components of the electrolyte are oxidized at high potentials and part of the metallic ions present in the positive electrodes are dissolved in the electrolyte[1] and migrate towards the negative electrode. As a result, electrolyte, electrode and electrode/electrolyte interface properties are degraded and battery performances are strongly diminished. The use of alkylcarbonates, especially ethylene carbonate (EC), is based on the suitable properties of a solid electrolyte interphase (SEI) formed on the negative electrode (e.g. graphite, Gr). Unlike, the surface film formed on the positive electrode is unstable, being grown, oxidized or decomposed at different stages of the charge/discharge. The addition to the electrolyte of SEI builders, mainly based on vinyl and heterocyclic compounds or inorganic salts, can improve the quality and stability of the films formed at both, negative and positive electrodes and enhances the battery cycling life. In order to get information on mechanism involved in the formation of the passivation layer on graphite electrodes, Li/Gr half cells and Gr/Gr symmetrical cells[2] (see Figure 1) have been studied by means of electrochemical impedance spectroscopy[3] and cyclic voltammetry. Single alkyl carbonate solvents are firstly introduced. Binary mixtures without and with additives have also been investigated. The study is completed by determining the nature of the electrolyte degradation products formed upon cycling by post-mortem analysis using CGMS.

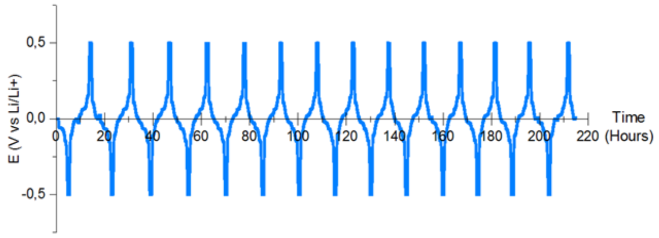


Figure 1 : Cycle performance at C/10 rate of Gr/Gr symetric cell containing DMC/LiPF6 1M at 20°C

[1] N. P. W. Pieczonka, Z. Y. Liu, P. Lu, K. L. Olson, J. Moote, B. R. Powell and J. H. Kim, *The Journal of Physical Chemistry C* **2013**, 11.

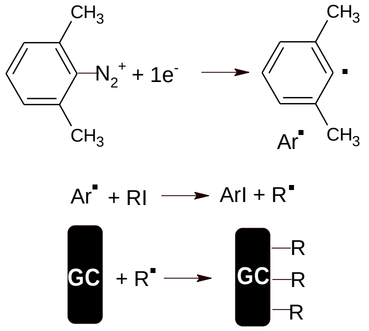
[2] J. Demeaux, E. De Vito, M. Le Digabel, H. Galiano, D. Lemordant and B. Claude-Montigny, *ECS Transactions* **2013**, *53*, 5-21.

[3] R. Petibon, N. N. Sinha, J. C. Burns, C. P. Aiken, H. Ye, C. M. VanElzen, G. Jain, S. Trussler and J. R. Dahn, *Journal of Power Sources* **2014**, *251*, 187-194.

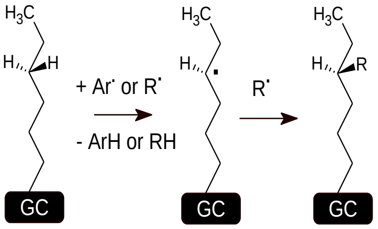
Electrografting of Alkyl Films at Low Driving Force by Diverting the Reactivity of Aryl Radicals Derived from Diazonium Salts.

Fetah I. Podvorica,[a,b] Dardan Hetemi,[a,b] Frédéric Kanoufi,[a] Catherine Combellas,[a] and Jean Pinson[a]
[a] Univ Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS
15 rue J-A de Baïf, 75205 Paris Cedex 13, France.
[b] University of Prishtina, Chemistry Department of Natural Sciences Faculty
rr. "Nëna Tereze" nr. 5, 10000 Prishtina, Kosovo.
fetah.podvorica@uni-pr.edu

The strategy consists in diverting the reactivity of aryl radicals obtained from diazonium salts towards the generation of reactive aliphatic radicals. This strategy is important in homogeneous synthesis[1-3] and was recently transposed to surface chemical functionalization by exploiting H atom transfer abstraction[4] or atom transfer reaction. Among diazonium salts, the 2,6-DMBD presents a special behavior since due to steric hindrance, the 2,6-dimethylphenyl radical (2,6-DMPh$^•$) cannot bind to surfaces as other aryl radicals do.[5] Such lack of reactivity should allow 2,6-DMPh$^·$ abstracting an iodine atom from an iodoalkane (RI),[6] mediating the generation of R$^•$ that attaches to the surface of glassy carbon to give stable alkyl monolayers that can be compared to thiol SAMs. Together with the positive shift of the potential for R$^•$ generation (-0.2$_5$ V/Ag/AgCl instead of -1.9 V/Ag/AgCl by direct electrografting of RI), its reduction to an unreactive anion is also greatly decreased. The alkyl chains are strongly attached as the grafted film withstands harsh rinsing. Finally, mono or multilayers can be obtained.[7]



Grafting of alkyl or perfluoroalkyl films



Formation of a multilayer

This strategy can be extended to bromoalkyl derivatives, leading to a higher positive shift (2.3 V instead of 1.7 V). It can also be extended by using a reducing agent in solution instead of an electrode, in order to graft other nanomaterials. Finally, the chemistry of aryl radicals may be driven through different ways to a variety of differently modified interfaces.

---

(1) Hari, D. P.; Hering, T.; König, B. *Angew. Chem. Int. Ed.* **2014**, *53*, 725-728.
(2) Heinrich, M. R. *Chem. Eur. J.* **2009**, *15*, 820-833.
(3) Hazimeh, H.; Piogé, S.; Pantoustier, N.; Combellas, C.; Podvorica, F. I.; Kanoufi F. *Chem. Mater.* **2013**, *25*, 605–612.
(4) Berisha, A.; Combellas, C.; Kanoufi, F.; Pinson, J.; Ustaze, S.; Podvorica, F. I. *Chem. Mater.* **2010**, *22*, 2962-2969.
(5) Combellas, C.; Jiang, D.; Kanoufi, F.; Pinson, J.; Podvorica, F. I. *Langmuir* **2009**, *25*, 286-293.
(6) Li, C. Halogen and chalcogen transfer chemistry in encyclopedia of radicals in chemistry, Biology and materials Vol. 2 (Eds.: C. Chatgilialoglu, A. Studer), John Wiley and Sons, New York, 2012, pp. 943–964.
(7) Hetemi, D.; Kanoufi, F.; Combellas, C.; Pinson, J. ; Podvorica, F. I. *Langmuir* **2014**, 30, 13907-13913.

Looking Closely at Magnesium Corrosion: Electrochemical Methods, Real-Time Optical Imaging and Hydrogen Measurement

M.Curioni
Corrosion and Protection Centre, School of Materials, The University of Manchester
Oxford Road, M13 9PL, Manchester, UK
Michele.curioni@manchester.ac.uk

Magnesium and magnesium alloys display relatively poor corrosion resistance compared to most other engineering alloys and present a relatively complex corrosion behavior. In particular magnesium exhibits the so called 'negative difference effect', i.e. an increase in the rate of hydrogen evolution with increasing anodic polarization. Further, during corrosion, its surface appearance progressively changes from silvery to dark, and the two of surfaces have significantly different electrochemical behaviors.

For these reasons, the evaluation of corrosion rate by electrochemical methods is not trivial. In order to elucidate these aspects, real-time hydrogen measurement, was performed simultaneously with potentiodynamic polarization or electrochemical impedance spectroscopy and real-time surface imaging. Potentiodynamic polarizations indicate that the electrical behavior deviates significantly from linearity even for small (±10 mV) polarizations with respect to the corrosion potential. Although this would suggest that estimation of values of corrosion rate from the values of resistances obtained by EIS is unreliable, since the assumption of linearity during EIS measurement is violated, an excellent correlation between the reciprocal of the resistances, estimated by EIS, and corrosion rate, obtained from real-time hydrogen measurement, is experimentally obtained.

The findings from electrochemical testing are complemented by relatively high-magnification in-situ optical imaging (~200 x) of the top view (Fig. 1a) and cross section (Fig. 1b) of corroding magnesium electrodes. From the images, it is evident that, initially, large hydrogen bubbles are generated on the silvery surface at specific locations, probably corresponding to iron-rich intermetallics. Such bubbles are stable and grow relatively slowly. Once corrosion is initiated, a continuous stream of small bubbles is observed everywhere on the propagating corrosion front, located at the interface between silvery and dark regions. Behind the corrosion front, the hydrogen evolution activity decreases with time, and bubbles are again generated only from specific locations. In addition, the formation of gels is directly observed above the dark corroded regions.

The findings suggest that pH increase due to hydrogen evolution plays a substantial role in the overall behavior: corrosion propagates towards the regions of lower pH, and vigorous hydrogen evolution is observed when the original air formed oxide/hydroxide film is disrupted. Subsequently, hydrogen evolution results in a pH increase that promotes the formation of a more passive film on the dark regions and the formation of gels. This suggests that corrosion propagates by disruption of the air-formed oxide-hydroxide layer and that, at the propagating front, the hydrogen evolution takes place on the exposed magnesium surface. With time, pH increases and a relatively protective film forms behind the corrosion front, hindering the homogeneous hydrogen evolution. On the dark regions far from the corrosion front, probably due to local compositional differences, i.e. as presence of intermetallics or regions of enriched alloying elements, hydrogen evolution again occurs only at specific locations.

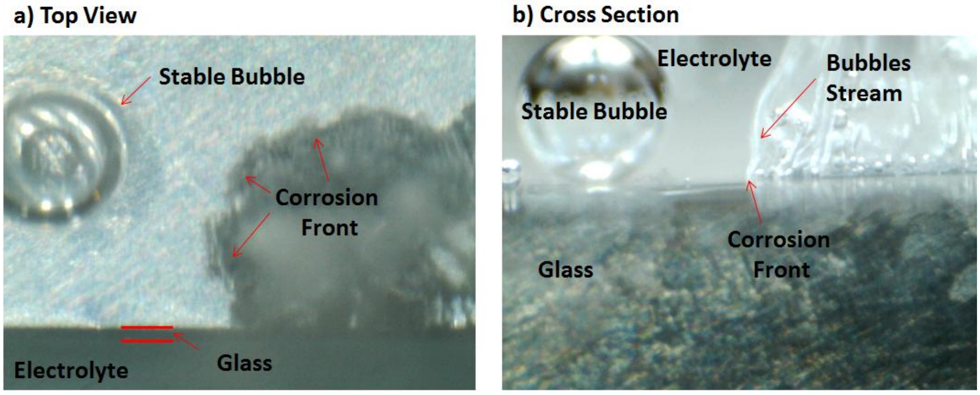


Figure 1: a) Top view and b) cross section of the corroding magnesium surface in 3.5% NaCl

Biomimetic Membranes and Characterization of Transport of Biochemically Important Species across them

Tomáš Navrátil [a], Kateřina Nováková [a], Ivana Šestáková [a], Romana Sokolová [a],
Jan Langmaier [a], Jana Jaklová Dytrtová [b]
[a] *J. Heyrovský Institute of Physical Chemistry of the AS CR, v.v.i.,*
Dpt. of Biomimetic Electrochemistry, Dolejškova 3, 182 23 Prague 8, Czech Republic
E-mail: Tomas.Navratil@jh-inst.cas.cz
[b] *Institute of Organic Chemistry and Biochemistry of the AS CR, v.v.i., Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic*

Phospholipid membranes (PLMs) surround every animal or plant cell and some subcellular organelles. Many elements and compounds, which are involved in biochemical pathways, have to be transported across them, i.e., from extracellular to intracellular fluid. On the contrary to many transported species, which are necessary for our life, also many undesirable and for cell health dangerous compounds and species are transported into the cells, where they start their negative activities. Transport of common species (glucose, calcium, sodium, etc.) is known in details. However, the transporting processes of hazardous species have remained unelucidated.

We have studied and simulated the transporting processes across a few types of supported biomimetic membranes: model (composed from phospholipids (PLs) and artificial ionophores) [1], mixed (composed from PLs and cholesterol [2], real transporters, parts of protoplasts [3]), and real membranes (composed of plant protoplasts [3]) and also unsupported liposomes (composed from PLs only) [4]. Some different methods of protoplasts preparation from leaves and roots of tobacco, of barley, and of potato have been tested and modified [3]. The used biomimetic membranes have been created in pores of different diameters of a polycarbonate substrate, which was fixed in specially developed electrochemical cells [1, 5].

The attention has been paid to the transport of hazardous metals (e.g., Cu, Cd) [3], low molecular weight organic acids (LMWOAs) (oxalic, citric, malic) [5], and phytochelatin PC_2.

The formed membranes have been characterized using electrochemical impedance spectroscopy (EIS) [2], optical microscopy, fluorescence microscopy, atomic force microscopy (AFM). Electrospray ionization – mass spectroscopy (ESI-MS) and hyphenated electrochemical cell placed prior this ESI–MS device have been applied for studies of transported complexes among hazardous metals and LMWOAs as well as for investigation of composition and structure of complexes formed among heavy metals (e.g., copper, ytterbium) and PLs creating the biomimetic membrane [6, 7]. Quantitative and qualitative analysis of transported time-stable species (ions, complexes, etc.) have been realized voltammetrically.

Acknowledgements

The research was supported by GA CR (project No. P208/12/1645) and by Academy of Sciences of the Czech Republic (project No. M200401201).

References

[1] T. Navratil, I. Sestakova, K. Stulik, and V. Marecek, Electroanalysis 22 (2010) 2043.
[2] K. Novakova, T. Navratil, I. Sestakova, V. Marecek, and J. Chylkova, Chemicke Listy 108 (2014) 219.
[3] K. Novákova, T. Navratil, I. Sestakova, M. P. Le, H. Vodickova, B. Zamecnikova, R. Sokolova, J. Bulickova, and M. Gal, Monatshefte Fur Chemie (2015) Accepted; DOI 10.1007/s00706.
[4] M. Parisova, T. Navratil, I. Sestakova, and V. Marecek, in XXXIII Moderni Elektrochemicke Metody (Modern Electrochemical Methods XXXIII) 2013 Eds: T. Navratil, M. Fojta, and K. Peckova), Best servis, Jetrichovice, pp. 139.
[5] M. Parisova, T. Navratil, I. Sestakova, J. Jaklova Dytrtova, and V. Marecek, International Journal of Electrochemical Science 8 (2013) 27.
[6] J. Jaklova Dytrtova, M. Jakl, K. Novakova, T. Navratil, and V. Sadek, Monatshefte fur Chemie (2015) Accepted; DOI 10.1007/s00706.
[7] J. Jaklova Dytrtova, T. Navratil, and V. Marecek, Collection of Czechoslovak Chemical Communications 76 (2011) 1917.

In-situ AFM studies of hydration effect at sputtered iridium dioxide thin films

Vitali Grozovski[1,2], Ilya Pobelov[1], Akiyoshi Kuzume[1], Tavo Romann[2], Enn Lust[2]
[1] Department of Chemistry and Biochemistry,
University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland
[2] Institute of Chemistry, University of Tartu,
14A Ravila Street, 50411 Tartu, Estonia
vitali.grozovski@dcb.unibe.ch

In-situ electrochemical AFM method was used for morphology investigation of reactively sputtered IrO_2 thin films [1,2] during oxygen evolution reaction (OER) in 0.1 M H_2SO_4 aqueous solution. IrO_2 film of 100 nm thickness was obtained by reactive magnetron sputtering in Ar/O_2 plasma at 3 mTorr chamber pressure, 60W RF source and implementing 2 inch Ir target. Substrate (glass plate) temperature was fixed at 300^o C.

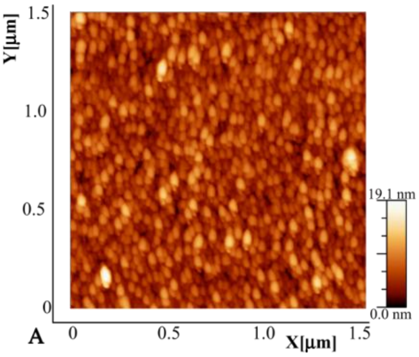


Figure 1. AFM image of IrO_2 thin film.

Relatively flat surface with pronounced grainy structure of sputtered IrO_2 was observed (Fig. 1), which was similar to previously reported [2,3] results for sputtered IrO_2. Roughness analysis gave root mean square roughness value (RMS) of 2.3 nm. The average grain size is 38 nm and average height of grains is 5 nm. Under electrochemical conditions in 0.1 M H_2SO_4 electrolyte solution and potential, E = 600 mV vs SHE, the surface of IrO_2 film became more expanded in three dimensions, but still regular structures were observed. Similar and slightly lower roughness values were obtained for this surface (RMS = 2.0 nm) and the average height of the grains stayed in 10 nm range. This phenomenon can be explained as oxide hydration process [2,4], where surface structures grow spatially. The observed regular structure did not change upon potential scan in both cathodic and anodic directions. Moreover under OER conditions and high anodic currents ($0.622\ mA \cdot cm^{-2}$) surface structure did not show any further reconstruction or alteration.

The hydration process of sputtered IrO_2 film was also studied in ultrapure water at open circuit potential. During this procedure IrO_2 sample was submerged into ultrapure water and series of AFM images were recorded as function of time. The formation of hydrated grainy structures was observed. After 120 min the surface of hydrated IrO_2 had the same structure as in the first experiment under electrochemical conditions.

These data are particularly interesting, as the hydration process is observed in-situ and from the starting point of the submersion of IrO_2 film into water medium.

Additional study implementing Raman spectroscopy was performed. Raman spectra were obtained at the surface and from the bulk of dry and wet IrO_2 films. In all cases three characteristic Raman shift peaks for IrO_2 were observed (362, 556 and 741 cm^{-1}), indicating to clean IrO_2 material with polycrystalline structure [3,5].

[1] E. Slavcheva, I. Radev, S. Bliznakov, G. Topalov, P. Andreev, E. Budevski, Electrochimica Acta. 52 (2007) 3889–3894.

[2] E. Slavcheva, R. Vitushinsky, W. Mokwa, U. Schnakenberg, J. Electrochem. Soc. 151 (2004) E226–E237.

[3] P.C. Liao, C.S. Chen, W.S. Ho, Y.S. Huang, K.K. Tiong, Thin Solid Films. 301 (1997) 7–11.

[4] S. Hackwood, L.M. Schiavone, W.C. Dautremont-Smith, G. Beni, J. Electrochem. Soc. 128 (1981) 2569–2573.

[5] P.C. Liao, W.S. Ho, Y.S. Huang, K.K. Tiong, J. Mater. Res. 13 (1998) 1318–1326.

In-operando electrochemical-surface plasma resonance (EC-SPR) observation to the kinetic study of solid electrolyte interface (SEI) formation on lithium ion battery

Fu-Ming Wang
National Taiwan University of Science and Technology
43 Keelung Road, Section 4, Taipei 106, Taiwan, R.O.C.
mccabe@mail.ntust.edu.tw

A novel *in-operando* observation to the formation of solid electrolyte interface (SEI) has been developed. This research demonstrates that the electrochemical-surface plasma resonance (EC-SPR) is able to evaluate the step-by-step kinetic molecule interaction between the electrolyte and the surface of electrode material. In this study, a commercial electrolyte (1M $LiPF_6$ into EC/EMC) has been used to define the SEI formation on gold (Au) electrode. Fig. 1a shows the linear sweep voltammogram (LSV) spectrum was operated at the scanning rate of 0.83 mV/s and in the operation window of 0~(-3) V. This result confirms that the SEI was formed at -1.24V and the lithium ion was going to reduce at -3V, indicating there are at least two passivation processes on this system. Fig. 1b shows a decreasing behavior of intensity difference of SPR, indicating the substances gradually covered for the Au electrode's surface. In accordance with Fig. 1b, this spectrum can be simply separated by two slopes. The two slopes cross a point at 21.5 min, representing the reduction time of SEI. Fig. 1c also illustrate a decreasing behavior of the angle difference of incidence, indicating a continually dissociation process was taking place. However, three different slopes were discovered and strongly correlated to the result in Fig. 1b. The first slope in Figs. 1b and 1c indicate the lithium ions dissociate from ethylene carbonate (EC) molecules and moves to the Au surface when the electrochemical driving force was triggered. The second slope in Figs. 1b and 1c implies an association process (a stable intensity in Fig. 1b and a lower slope in Fig. 1c), indicating that the lithium ion joins the SEI formation at typical reduction potential on Au surface. However, Fig. 1c reveals that the Au electrode is not able to correlate the SEI formation due to the slope changes into higher value (third slope), which represents the intrinsic property of Au is different to graphite [1], implying the SEI is further dissociated from Au surface. The SEI formation on typical electrode materials such as graphite, graphene, and silicone are under researching.

The EC-SPR is a powerful instrument for studying the SEI in order to character an in-operando interaction mechanism between the electrolyte molecules and electrode materials.

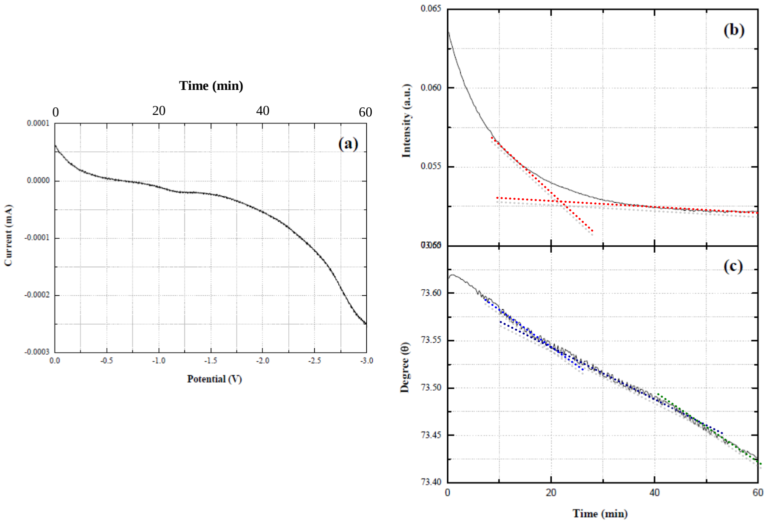


Fig. 1 *In-operando* EC-SPR observations of (a) the LSV, the sensograms of (b) the intensity difference of SPR, and (c) the angle difference of incidence.

Reference

[1] S. S. Zhang, J. Power Sources 162 (2006) 1379.

Electrochemical corrosion behavior of S32750 super duplex stainless steel in NaCl solution

Lijing Yang, Jin HE, Masoumeh Moradi, Zhenlun Song
Key Laboratory of Marine New Materials and Related Technology
Zhejiang Key Laboratory of Marine Materials and Protection Technology
Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences
Ningbo, 315201, P.R. China
e-mail:yanglj@nimte.ac.cn

Abstract: The electrochemical corrosion behaviour and critical pitting temperature (CPT) of S32750 super duplex stainless steel (SDSS) in 3.5% NaCl solution were investigated by electrochemical techniques. The morphologies of the matrix and pits were observed by scanning electron microscope. The CPT of the S32750 steel was identified at 71℃. The passive film could be formed on the specimen surface when the solution temperature was lower than the CPT. While, when the solution temperature was above the CPT, pitting corrosion occurred on the specimen surface as the activity of Cl^- increased and the passive film dissoluted. Pitting corrosion became more serious with the temperature increased. Moreover, the corrosion models of the steel below and above the CPT were sketched respectively.

Key words: duplex stainless steel; critical pitting temperature; passivation; corrosion

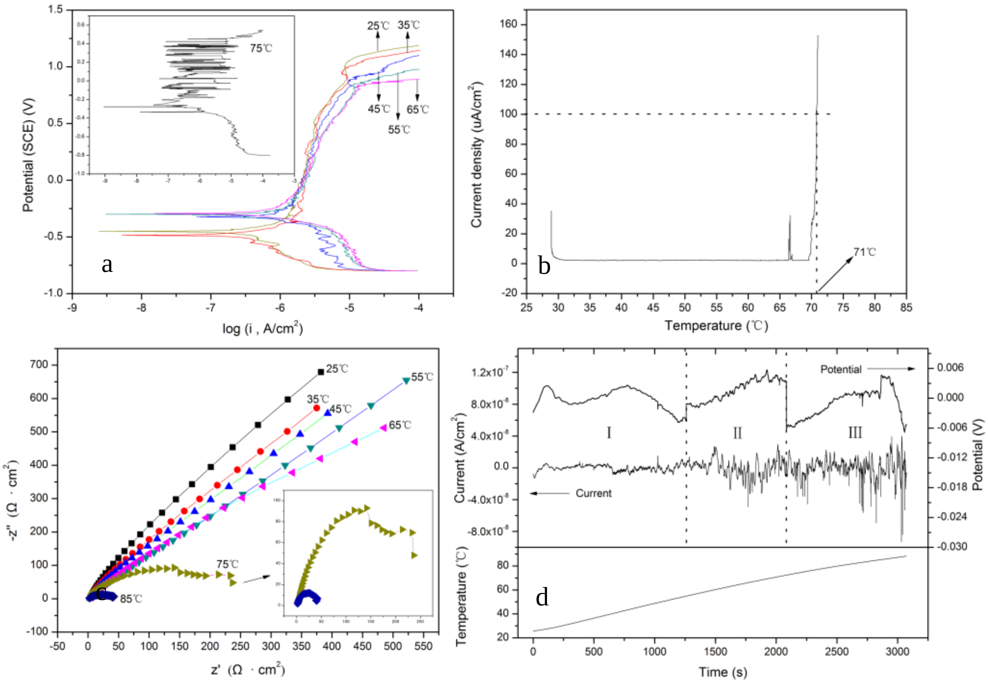


Fig. 1 The electrochemical results of the SDSS measured with various temperatures: (a) polarization curves;(b) I-T curve; (c) EIS; (d) Electrochemical noise

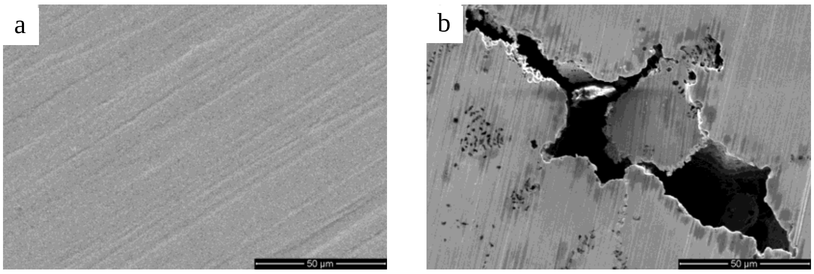


Fig. 2 Surface morphology of the samples after EIS test at different temperatures: (a) 65℃, (b)85℃.

A Multi Length Scale Study of Cathodic Disbondment from Tin and Iron-Tin Intermetallic Coated Steel.

N.Wint[a], H.N.McMurray[a], S.Geary[a] and A.C.A. de Vooys[b]
[a]Swansea University [b]Tata Steel
[a]School of Engineering, Swansea University, Singleton Park, Swansea, UK, SA2 8PP
[b]Tata Steel Research and Development, PO BOX 10.000, 1970 CA Ijmuiden, The Netherlands.
483404@swansea.ac.uk

This paper describes a systematic study into the kinetics and mechanism of cathodic disbondment affecting polyvinyl butyral (PVB) on pure iron, pure tin and industrially important tin and iron-tin intermetallic (FeSn and $FeSn_2$) coatings used for packaging steels as a function of coating weight.

Tin and iron-tin intermetallic coated samples were obtained from Tata Steel. In all cases the tin layer had been produced by electrodeposition. When required the tin coated samples had subsequently been heated to produce FeSn and $FeSn_2$ layers by thermal inter-diffusion.

Metallic sample coupons were solvent coated with a 30µm layer of PVB. Corrosion driven cathodic disbondment of the PVB lacquer was then studied using a Stratmann type delamination cell in conjunction with 5% aqueous NaCl (1, 2).

The time dependent extent of delamination was determined by repeated in situ scanning using a scanning Kelvin probe (SKP) apparatus. The capability of the SKP to visualize the spatial distribution of localized free corrosion potential variation with time has been demonstrated previously (1, 2).

Delamination was not observed on pure tin or tin coatings but was found to occur at reduced rates on both FeSn and $FeSn_2$ intermetallics, when compared with pure iron. Negligible change in rate was observed when varying coating weight.

Results are explained in terms of electrocatalytic activity for the cathodic oxygen reduction reaction (ORR) using results obtained from a rotating disk electrode (RDE). It is concluded that the lack of cathodic disbondment in the case of tin coatings, and decreased rate of propagation, when compared to iron, in the case of iron-tin intermetallics is due to the high overpotential for the ORR associated with tin (3).

In conclusion macro electrochemical RDE results obtained correlate with delamination studies conducted on the millimeter scale and show that the rate of cathodic delamination of an organic coating from a material is determined by its electrocatalytic activity for the ORR. Electron microscope images obtained on the micron scale have been used to confirm that although subsequent anodic attack may occur due to the alkaline nature of the underfilm electrolyte, anodic activity is not considered to be rate determining (2).

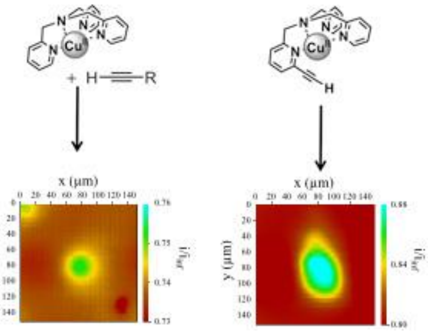
References

1.) M. Stratmann, H. Streckel, R. Feser, A new technique able to measure directly the delamination of organic polymer films, Corrosion Science 32 (1991) 467.
2.) A. Leng, H. Streckel, M. Stratmann, The delamination of polymeric coatings from steel. Part 1: Calibration of the Kelvinprobe and basic delamination mechanism, Corrosion Science 41 (1999) 547.
3.) I. A. Ammar, S. Darwish, M. W. Khalil, A. Galal, Potentiodynamic and cyclic voltametric studies on the passivity of tin in neutral phosphate buffer, Z.Werkstofftech 16 (1985) 194.

Locally Self-induced “electro-click” onto self-assembled monolayer: Evidence for surface self-catalysis propagation

Sébastien Lhenry[a], Yann R. Leroux[a], Christophe Orain[b], Francoise Conan[b], Nathalie Cosquer[b], Nicolas Le Poul[b], Yves Le Mest[b], O. Reinaud[b], Philippe Hapiot[a]
[a]*Institut des Sciences Chimiques de Rennes, CNRS, Université de Rennes 1*
[b]*CEMCA, Université de Bretagne Occidentale, Brest*
[c]*LCBPT, Université Paris Descartes, France*
yann.leroux@univ-rennes1.fr

In this communication, observation of a 2D self-propagation catalytic reaction on surfaces is described. Huisgen 1,3-dipolar cycloaddition, known as click chemistry[1], is one of the most used catalytic reaction nowadays as it is a highly versatile and fast coupling reaction. It can be used as well with biological samples in water or in classic organic synthesis. In parallel, interest in chemically modified surfaces has been growing for several decades due to their many applications in various scientific areas. Among many methods to chemically modified surfaces, click chemistry coupling is also often used for its efficiency and its great selectivity. This coupling reaction between an azido and a free alkyne is catalyzed by Cu(I) which can be generated chemically or electrochemically, leading to “electro-click chemistry reaction” in the latter case. Recently, using Scanning Electrochemical Microscopy (SECM), localized electro-click chemistry reactions were successfully performed.[2] “Self-induced” electro-click chemistry reaction can be achieve when using a molecule that is at the same time a reactant and the catalyst.[3] In this communication, we will specifically study local self-induced electro-click chemistry reaction onto self-assembled monolayers by SECM. It will be demonstrated that using this specific class of molecule (see scheme), catalytic properties can be transferred to the surface and that 2D self-propagation of the catalytic reaction on the surface can be seen. Particular attention will be paid to the determination of the experimental conditions needed to performed and monitored these experiments in unbiased conditions (the substrate is not electrically connected).[4]



[1] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless. A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective “Ligation” of Azides and Terminal Alkynes, Angew. Chem., Int. Ed. 41 (2002) 2596.

[2] D. Quinton, A. Maringa, S. Griveau, T. Nyokong, F. Bedioui, Surface patterning using scanning electrochemical microscopy to locally trigger a “click” chemistry reaction, Electrochem. Com. 31 (2013) 112.

[3] A. Gomila, N. Le Poul, N. Cosquer, J.-M. Kerbaol, J.-M. Noël, M. T. Reddy, I. Jabin, O. Reinaud, F. Conan, Y. Le Mest, Self-induced “electroclick” immobilization of a copper complex onto self-assembled monolayers on a gold electrode, Dalton Trans 39 (2010) 11516.

[4] S. Lhenry, Y. R. Leroux, C. Orain, F. Conan, N. Cosquer, N. Le Poul, O. Reinaud, Y. Le Mest, P. Hapiot, Locally Induced and Self-Induced “electro-click” onto Self-Assembled Monolayer: Writing and Reading with SECM under Unbiased Condition, Langmuir 30 (2014) 4501−4508.

SKP and EIS Characterization of the passivity 301 Stainless Steel under Mechanical Stress.

Nuria Fuertes Casals[1], Andrei Nazarov[2], Flavien Vucko[2], Dominique Thierry[2]
[1]*SwereaKIMAB AB, Stockholm, Sweden*
[2]*French Corrosion Institute, Brest, France*
Andrej.nazarov@institut-corrosion.fr

The Kelvin Probe (vibrating capacitor) technique is often applied to measure the Volta potential of an electrode (Φ_w/e) relatively to any reference electrode or the electron work function (Φ) relatively to the zero level in vacuum. SKP determines the Volta potential difference between the probe and the working electrode surface according to:

$$\Delta V_{p/w} = (\Phi_w - \Phi_P) / e \qquad (1),$$

where e is an electron charge. Keeping the potential of the probe (Φ_p/e) constant and calibrated the potential (Φ_w/e) of the steel surface can be obtained. Φ is defined as the minimum energy required for extracting an electron from a metal to a distance close to the surface. It relates to the potential of an electron (1,2).

$$\Phi = \Phi_v - \mu_e \qquad (2),$$

where (Φ_v) is the electrostatic potential in the vacuum and (μ_e) is the chemical potential of an electron in the metal.

$$\Phi = \mu_e - e\,\chi \qquad (3).$$

Φ can be subdivided for two contributions (equation 3) including the metal bulk (chemical potential of the electron, μ_e) and surface depended contribution related to the potential drop at the metal-vacuum interface (χ). For metal covered by semiconducting oxide film the potential drop across the metal-oxide-air interfaces (χ_{sc}) depends on the difference in Fermi levels in the metal (μ_e) and in the oxide (E_F), electron bands bending in the oxide ($\Delta\chi_{ox}$) due to adsorption phenomena and the formation of a dipole layer ($\beta_{ox/air}$) on the oxide surface (4):

$$\chi_{sc} = (E_F - \mu_e)/e + + \Delta\chi_{ox} + \Delta\chi_{air} \qquad (4)$$

$$\Phi/e = \mu_e / e + \Delta\chi_{ox} + \Delta\chi_{air} = \mu_e/e + q/C_{ox} + q/C_{air} \qquad (5)$$

The potential drops in the oxide and double electric layer are related to the corresponding capacitances (C_{ox}, C_{air}) and the electric charge (q). From equation 5, the electrochemical potential is reciprocal to capacitance of the oxide film.

Scanning Kelvin Probe (SKP) was applied in ambient air to study the impact of elastic and plastic strain on the surface distribution of electrochemical (Volta) potential of stainless steel 301LN grade. EIS was applied in aqueous electrolyte to measure the influence of the stress on the oxide film capacitance to validate equation (5). Plastic tensile deformation resulted in the formation of dislocations and pile-ups of dislocations that was visualized by AFM. The oxide film was also characterized by XPS.

It was shown that localized tensile and compressive stress decreased the electrochemical potential and the level of steel passivity. This effect is explained by the formation of dislocations that create defective oxide films with a resulting decrease in the ability to passivation.

Scanning elctrochemical microscopy of interfaces in lithium-ion and metal-air batteries

G. Wittstock,[1] H. Bülter,[1] F. Peters,[2] J. Schwenzel[2], P. Schwager[1,2], I. Plettenberg[1]

1 Carl von Ossietzky University of Oldenburg, Department of Chemistry, D-26111 Oldenburg, Germany
2 Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Wiener Strasse 12,
D-28359 Bremen, Germany
gunther Wittstock@uni-oldenburg.de

In our society Li ion batteries are widely used. Mainly during the first charging process the solid electrolyte interphase (SEI) between the electrode and electrolyte is formed by the decomposition of electrolyte components at the lithiated graphite. This layer is critical for the performance and safety of the Li ion batteries [1]. The aim of this study is to characterize the electron transport across the SEI, which determines the ongoing reduction of electrolyte components. Thus, understanding the electron transport across the SEI helps to improve lithium ion batteries.
Characterization of the SEI is a challenge, because of the variety of chemically similar components and enclosed electrolyte species. Furthermore, *ex situ* analysis of the SEI requires separation and isolation of the SEI, which may change the content and the structure of the SEI [2]. Recently we used the feedback mode of scanning electrochemical microscopy (SECM) to investigate *in situ* the electron transport at the lithiated graphite (Figure) [3]. 2,5-di-*tert*-butyl-1,4-dimethoxy benzene was identified as an useful SECM mediator providing sufficient stability and sensitivity passivation properties of SEI. All measurements were conducted under open circuit conditions. Our results by SECM show gradual and significant short-term *spatiotemporal* changes of the SEI properties and demonstrate the dynamic and spontaneous behavior of SEI formation, damage and reformation under open circuit conditions above lithiated graphite anodes. The results emphasize that *spatiotemporal* changes of the passivating SEI properties are highly localized and occur preferentially in between the gaps of graphite particles. Significant short-term *spatiotemporal* changes of the SEI properties clarifies that electrolyte reduction still occurs after SEI formation at localized spots.

Using a related setup, Gas permeation though an gas-diffusion electrode (GDE) into an Li^+-containing electrolyte has been studied in order to understand pore blocking vs. electrode coating by lithium oxides during the operation of lithium-air batteries [4]. The GDE was positioned between an Ar-O_2 and an Ar atmosphere. The passivation of the local detector electrode was avoided by the use of a pulse program that contained a cleaning step for the microelectrode. The difference in O_2 partial pressure was the driving force for the transport of O_2 through the wetted pore structure of the GDE. Depending on the potential of the GDE O_2 enters the organic electrode or is completely consumed in the GDE. In this way it was possible to detect the build up of concentration gradients in the electrolyte above an GDE in organic electrolytes in dependence of the operation characteristics of the air cathode. Intermediates of the oxygen electrode have been detected but have not yet been chemcially identified.

[1] S. Krueger, R. Kloepsch, J. Li, S. Nowak, S. Passerini, M. Winter, J. Electrochem. Soc. 160 (2013), A542.
[2] P. Verma, P. Maire, P. Novak, Electrochim. Acta 55 (2010) 6332.
[3] H. Bülter, F. Peters, J. Schwenzel, G. Wittstock, Angew. Chem. Int. Ed. 53 (2014) 10531.
[4] P. Schwager, D. Fenske,. G. Wittstock, J. Electroanal. Chem (2015) in press.

Efficient FTO-Free Cathode for Dye-Sensitized Solar Cells

Ladislav Kavan[1,2*], Paul Liska[2], Shaik M. Zakeeruddin[2] and Michael Graetzel[2]
[1]J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic,
Dolejškova 3, CZ-18223 Prague 8, Czech Republic
[2]Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Swiss Federal
Institute of Technology, CH-1015 Lausanne, Switzerland
e-mail: kavan@jh-inst.cas.cz

A traditional cathode in dye-sensitized solar cell (DSC) is platinized F-doped SnO_2 (FTO). However, the cost of FTO glass is estimated to be about >20-60% of the cost of the DSC-module, which is a strong motivation for FTO replacement by cheaper materials. Recently, nanocarbon and graphene-based materials attracted considerable attention, particularly for Co-mediated DSCs. Another alternative, which also works well with the I_3^-/I^- redox mediator, is the woven fabric consisting of transparent PEN fibers in warp and electrochemically platinized tungsten wires in weft. This electrode outperforms the thermally platinized FTO in serial ohmic resistance, R_s (1.5 vs. 8.2 Ωcm^2), charge-transfer resistance for triiodide reduction (0.59 Ωcm^2 vs. 0.76 Ωcm^2) and offers comparable or better optical transparency in the visible and particularly in the near-IR spectral region (≈80%). The Pt-W/PEN cathode exhibits good stability during electrochemical load with the maximum (diffusion-limited) current both in cathodic and anodic directions, and during long term (≈month) storage at open circuit. The practical dye-sensitized solar cells with either Pt-W/PEN or Pt-FTO cathodes show similar performance, confirming that the former is a promising alternative for replacement of conductive glass in the DSC counterelectrodes.

Acknowledgement: This research was supported by the Grant Agency of the Czech Republic (contract No. 13-07724S), by the Swiss Commission for Technology and Innovation (CTI) project No. 16452.2 PFNM-NM and by the European Research Council through the Advanced Research Grant no. 247404 'Mesolight'.

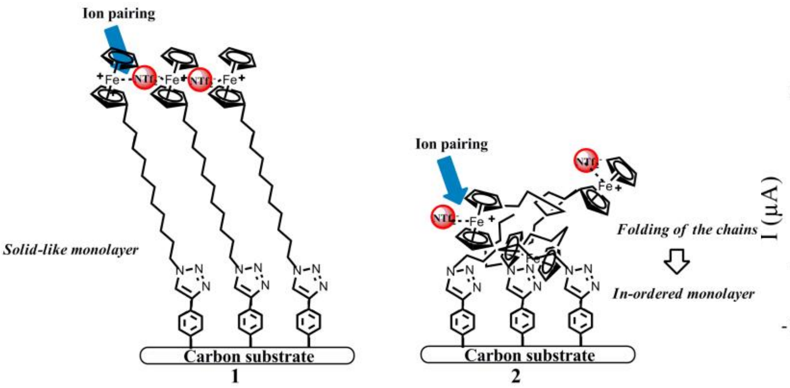
Comparative Electrochemical Investigations in Ionic Liquids and Molecular Solvents of a Carbon Surface Modified by a Redox Monolayer

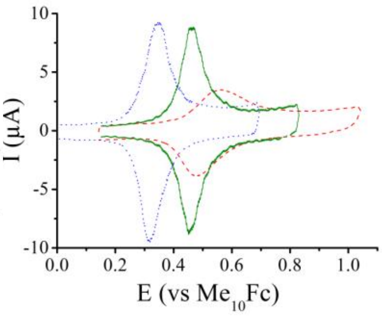
Joanna Jalkh, Yann R. Leroux, Corinne Lagrost, and Philippe Hapiot
Institut des Science Chimiques de Rennes, Université de Rennes1, CNRS, UMR 6226
(Equipe MaCSE)
Campus de Beaulieu, 35042 Rennes Cedex, France
Email: joanna.jalkh@univ-rennes1.fr

The preparation of robust modified surfaces with a molecular organization presents a growing interest for many applications ranging from analytical chemistry, molecular electronics, or more recently in charge storage devices as supercapacitors.[1] One of the well-known methods to form robust, covalently attached monolayers on various surfaces is the electroreduction of aryldiazonium salts[2]. Click chemistry allows the post-functionalization of the platform by functional entities[3]. Hence, covalently bonded ferrocene molecules were efficiently grafted on a carbon surface with long alkyl chain linkers[4].

A particular stability of our grafted monolayer encouraged us to perform kinetic and thermodynamic studies in room temperature ionic liquids (RTILs) and organic solvents (ethanol and dichloromethane). RTILs present large potential interest as solvents for electrochemical applications owing to their unique chemical and physical properties[5]. Despite the large literature on interfacial charge transfer, little is known about the basic properties of covalently bound electroactive monolayers in RTILs, especially how basic properties like stability or electrochemical behavior evolve when passing from a classical organic solvent to a RTIL. We observed that the kinetics of electron transfer is much slower in RTILs than in organic media due to the ordering present in RTILs. This communication presents a comparative study on the redox behavior of electrochemically active, covalently bonded ferrocene monolayer of nanometric thickness, on a carbon surface in RTILs and organic solvents.

Besides the anionic and cationic investigations showing the influence of viscosity and conductivity on the kinetic and thermodynamic aspects, an important phenomenon is the dynamic hysteresis which was observed in all of the RTILs by the appearance of asymmetric voltammograms. This phenomenon could be due to the formation of a solid-like monolayer or to a reorganization of the monolayer forming an inordered one, leading in both cases to a slower electron transfer.





Scheme 1 – Two possible explanations for the dynamic hysteresis interfering in the case of RTILs.

Scheme 2 – Behavior of the redox entities in Ethanol (dotted), dichloromethane (line) and $BMINTf_2$ (dashed) at 0.2 V/s.

[1] A. Devadoss, C. Chidsey, Azide-modified graphitic surfaces for covalent attachement of alkyne-terminated molecules by ‘Click’ chemistry, J. Am. Chem. Soc. 129 (2007) 5370.

[2] J. Pinson, F. Podvorica, Attachment of organic layers to conductive or semiconductive surfaces by reduction of diazonium salts, Chem. Soc. Rev. 34 (2005) 429.

[3] Y. Leroux, H. Fei, J-M. Noel, C. Roux, P. Hapiot, Efficient covalent modification of a carbon surface: Use of a silyl protecting group to form an active monolayer, J. Am. Chem. Soc. 132 (2010) 14039.

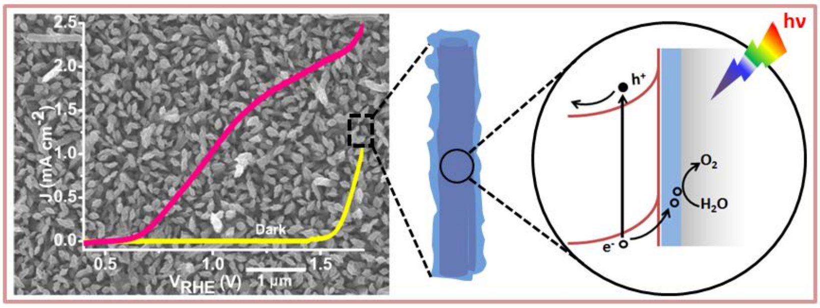
[4] J. Jalkh, Y. Leroux, C. Lagrost, P. Hapiot, Comparative electrochemical investigations in ionic liquids and molecular solvents of a carbon surface modified by a redox monolayer, J. Phys. Chem. C 118 (2014) 28640.

[5] V. Parvulescu, C. Hardacre, Catalysis in ionic liquids, Chem. Rev. 107 (2007) 2615.

Photoelectrochemical Water Splitting at Low Applied Potential Using NiOOH Coated Codoped (Sn, Zr) α-Fe_2O_3 Photoanode

Andebet Gedamu Tamirat[a], Wei-Nien Su*[b], Amare Aregahegn Dubale[a], Hung-Ming Chen[a], and Bing-Joe Hwang*[ac]
[a]*NanoElectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, 106, Taiwan. E-mail: bjh@mail.ntust.edu.tw, 10607*
[b]*NanoElectrochemistry Laboratory, Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan*
[c]*National Synchrotron Radiation Research Center, Hsinchu, 30076, Taiwan*

Abstract: One of the major challenges in photoelectrochemical water splitting is to develop an efficient photoanode that can oxidize water at low applied potential.[1] Herein, a codoped (Sn, Zr) α-Fe_2O_3 photoanode modified with stable and earth abundant nickel oxyhydroxide (NiOOH) co-catalyst that can split water at low applied potential is reported. First, unintentional gradient monodoped (Sn) Fe_2O_3 photoanode was synthesized at controlled annealing temperature that achieved a photocurrent density of 0.86 mA/cm^2 at 1.23 V vs. RHE. We have found that incorporation of gradient Sn doping results in the formation of upward multi band bending through building distributed n^+–n homojunctions.[2] Further doping with optimized amount of Zr outperformed the monodoped (Sn) Fe_2O_3 photoanode providing significantly much higher photocurrent density (1.34 mA/cm^2). The remarkably improved electrical conductivity and more than three times higher charge carrier density (as evidenced from electrochemical impedance spectroscopy measurements and Mott-Schotttky analysis) of the codoped (Sn, Zr) Fe_2O_3 photoanode highlights the importance of codoping.[3] The synergetic effect of codoping (Sn, Zr) led to 1.6 fold enhancement in charge separation efficiency at 1.23 V than that of the monodoped (Sn) Fe_2O_3 photoanode. The NiOOH modified codoped (Sn, Zr) α-Fe_2O_3 photoanode exhibited drastically lower onset potential (0.58 V) and a photocurrent density of 1. 64 mA/cm^2 at 1.23 V. Interestingly a 160 mV cathodic shift in photocurrent onset potential was also observed. Concomitant with this, the NiOOH modified codoped (Sn, Zr) Fe_2O_3 photoanode exhibited 1.6 to 9.5 fold enhancement in charge injection efficiency (η_{inj}) at kinetic control region of 0.7 to 0.9 V compared to unmodified codoped photoanode. Gas evolution measurements also showed that the NiOOH modified codoped Fe_2O_3 photoanode achieved an average Faradaic efficiency of 93%.



References

[1] M. Barroso, C.A. Mesa, S.R. Pendlebury, A.J. Cowan, T. Hisatomi, K. Sivula, M. Grätzel, D.R. Klug, J.R. Durrant, Proceedings of the National Academy of Sciences, 109 (2012) 15640-15645.
[2] F.F. Abdi, L. Han, A.H.M. Smets, M. Zeman, B. Dam, R. van de Krol, Nat Commun, 4 (2013) 1-5.
[3] B.A. Aragaw, C.-J. Pan, W.-N. Su, H.-M. Chen, J. Rick, B.-J. Hwang, Applied Catalysis B: Environmental, 163 (2015) 478-486.

Characterization of Corrosion-Resistant Aluminosilicate Coatings Prepared by Multiple Sol-Gel Spin Casting

Hiroki Habazaki[1,2], Taiki Kimura[2], Yoshitaka Aoki[1,2], Etsushi Tsuji[1,2], Takayoshi Yano[3],
Achim W. Hassel[4]
[1]Division of Materials Chemistry & Frontier Chemistry Center, Faculty of engineering,
Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
[2]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo,
Hokkaido 060-8628, Japan
[3]Steel Research Laboratory, JFE Steel Corporation, 1 Kawasaki-cho, Chuo-ku, Chiba 260-0835, Japan
[4]Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz, Altenberger
Strasse 69, 4040 Linz, Austria
habazaki@eng.hokudai.ac.jp

In this study, we demonstrate highly improved corrosion resistance of Type 430 stainless steel by multiple sol-gel spin coating of aluminosilicate using diluted precursor solutions. The coatings of ~65 nm thickness were prepared from the precursor solutions with the [Al+Si] = 50, 100 and 500 mM and [Al]/[Si]=1/4. After coating, the specimens were annealed in air at 400ºC. The coating prepared from the 50 mM precursor solutions was more dense and showed highly ennobled pitting potential higher than 1 V vs Ag/AgCl in 0.6 mol dm^{-3} NaCl aqueous solution, while the coating prepared from 500 mM precursor solution did not show obvious ennoblement of the pitting potential by the coating [1].

Flaws are present in the coated specimens. In order to examine whether pits are initiated at such flaws, a micro-droplet cell study was conducted. Even under the micro-droplet cell, the more ennoblement of the pitting potential by coating from more diluted solutions was observed at the flaw-free regions. In addition, no preferential pit initiation was found at the flaw regions when the coating was formed from the 50 mM precursor solution. Thus, the flaw regions of the stainless steel substrate were effectively covered by the coating. In contrast, when the coating was formed from the 500 mM precursor solution, pits were often formed at the flaw regions.

The coating insulating properties were also examined using a conductive AFM. The coatings before annealing in air were rather microscopically flat, but nanoscale roughness was introduced by annealing in air at 400ºC. The current image disclosed that the ridge regions were less insulating. From the low-voltage SEM and TEM observations, it was found that iron was oxidized and diffused into the coating surface locally, developing less insulating regions. It was also found that the oxidation of the stainless steel substrate was dependent upon its grain orientation even under the coating. All the coatings prepared from different precursor solutions showed similar morphology and conductivity, such that the coatings were not sufficiently dense to suppress the oxidation of substrate in air at 400ºC.

In conclusion, the multiple spin coating from diluted precursor solutions is effective in preparing a corrosion-resistant coating. Micro-droplet cell study is useful to examine the corrosion behavior of flaw-free and flaw-containing regions separately. Conductive AFM is powerful in examining the electric properties of the coatings in nanoscale resolution.

Reference

[1] H. Habazaki, T. Kimura, Y. Aoki, E. Tsuji, T. Yano, J. Electrochem. Soc., 161 (2014) C57-C61.

Thermodynamic Study of the Adsorption of Calf Thymus DNA at the Platinum/Buffer Electrolyte Interface.

L.M. Bravo-Anaya[1,2*], Y. Rharbi[2], N. Casillas[3], J.F.A. Soltero[1], E.R. Larios-Durán[1]
[1] Univ. Grenoble Alpes, LRP, F-38000 Grenoble, FRANCE.
[2] Universidad de Guadalajara. Departamento de Ingeniería Química y [3] Química, Blvd. M. García Barragán #1451, C. P. 44430, Guadalajara, Jalisco, MEXICO.
**monik_ayanami@hotmail.com*

Interactions between biological molecules with metal interfaces are of great interest in fundamental and biotechnological applications [1]. DNA, known as the most important biomolecule, has been studied in the field of linear polymers and is characterized by having three typical regimes, bounded by two critical parameters sensible to DNA conformation, i.e. the overlap (C*) and the entanglement (C_e) concentrations [2]. DNA chains interactions with charged surfaces determine and/or affect their biological functions in a different way at each characteristic regime. A thermodynamic analysis of differential double-layer capacity data [3] was carried out in order to describe Calf Thymus DNA (13 kbp) adsorption at the platinum electrode surface. The adsorption parameters such as Gibbs excess (Γ_{DNA-}) and Gibbs energy of adsorption (ΔG) were determined as a function of electrode potential and charge density for DNA concentrations from 0.01 to 2.5 mg mL^{-1}, at a temperature of 20 ºC and a pH of 7.3. DNA adsorption has been found very favorable at more positive potentials than 15 mV vs. SCE, related to the potential of zero charge of the interface [4]. Therefore, our results show that the adsorption of DNA presumably causes a positive charge to flow to the platinum side of the interface. The obtained values for the Gibbs excess show a quasi-parabolic dependence with potential at each characteristic regime. The strong interactions between DNA and platinum may be related to the absence of transitions on the Gibbs excess response as observed in other adsorption studies, such as for the PO_4^- [5]. DNA adsorption process was also monitored through EIS measurements that were carried out at open circuit potential. This response leads to an adsorption of DNA molecules onto the platinum electrode, allowing interpreting and analyzing the results in terms of the adsorption impedance theory by transforming them into complex capacitance data and using an equivalent circuit similar to the one proposed by FMGR [6]. DNA diffusion coefficients were calculated using the obtained parameters through both differential double-layer and impedance studies and were analyzed at each DNA characteristic regime.

Para ver esta película, debe
disponer de QuickTime™ y de
un descompresor .

Gibbs excess as a function of electrode potential for DNA adsorption at the Platinum /TrisHCl-EDTA Buffer interface.

[1] R.J. Green, R.A. Frazier, K.M. Shakesheff, M.C. Davies, C.J. Roberts, S.J.B. Tendler, *Biomaterials* **21**, 1823–1835, (2000).
[2] E. Raspaud, D. Lairez and M. Adam, *Macromolecules*, **28**, 927-933, (1995).
[3] Z. Shi and J. Lipkowski, *Journal of Electroanalytical Chemistry,* **403**, 225-239, (1996).
[4] L. M. Bravo-Anaya, E. R. Macías, F. Carvajal Ramos, J. G. Álvarez-Ramírez, *Journal of The Electrochemical Society*, **160** (4), G69-G74 (2013)
[5] J. Mostany, P. Martínez, V. Climent, E. Herrero and J. M. Feliu, *Electrochimica Acta*, **54**, 5836-5843, (2009).
[6] A. N. Frumkin, and V. O. Melik-Gaykazyan, 5, 855 (1951). *Dokl. Akad. Nauk,*, **5**, 855 (1951).

Calculation of effective transport and kinetic parameters of electrochemical energy conversion and storage devices at multiple length scales

A. Kriston, A. Pfrang, L. Boon-Brett
Institute for Energy and Transport, Joint Research Centre, European Commission,
1755 ZG Petten, The Netherlands
akos.kriston@ec.europa.eu

In this work experimental and numerical simulation techniques are used to understand how transport, and charge transfer processes are linked at different length scales in various power sources, such as batteries, fuel cells and supercapacitors. A general pore-scale model has been developed by mimicking the layer fabrication process[1]. Different electrode structures are generated taking into account the interaction between the deposited particles during layer formation and subsequent surface reorganization. Instead of simulating each generated layers at macro scale, scaling analysis was applied to reduce the complexity of the system. It is shown, that in spite of the diverse morphology, the generated layers belong to the same universality class and can be normalized by a self-affine transformation. A simple scaling function is introduced and the scaling exponents are determined for the different layer growth processes. By using these scaling exponents the effective transport and kinetic coefficients of the layers are calculated at different length scales and nested into macro homogeneous models to simulate polarization curves of fuel cells and supercapacitors and charge-discharge curves of Li-ion batteries.

The model prediction of mass activity of fuel cells and specific capacity of supercapacitors are compared with experimental data and a good agreement was found. The developed technique has been applied to elaborate the effect of Pt loading[2] of fuel cells. The experimental results indicates that, as Pt loading decreases from 0.4 to 0.05 mg cm^{-2}, the mass activity increases by a factor of 2.7, while at the same time the mass transport resistance increases. The self-affine scaling law, derived from our pore-scale model, is applied to experimental data and a good correlation is found between scaling exponents and transport properties. The technique is also applied for the optimization of novel Si and atomic layer deposited electrodes of Li-ion batteries. The volumetric energy, specific energy and power densities are calculated and an optimized layer fabrication process is determined.

The results of this comparison imply that porosity, tortuosity and specific surface area follow a non-linear scaling law with increasing deposited mass, which is not commonly considered in electrochemical systems. Consequently, the measured effective transport and kinetic coefficients at macro scales can differ from those determined at micro- or nano-scales, and depend on the volume or mass of the sample.

---

[1] Akos Kriston, Andreas Pfrang, Branko N. Popov, Lois Boon-Brett, Development of a full layer pore-scale model for the simulation of electro-active material used in power sources, Journal of The Electrochemical Society, 161 (8) E3235-E3247 (2014)

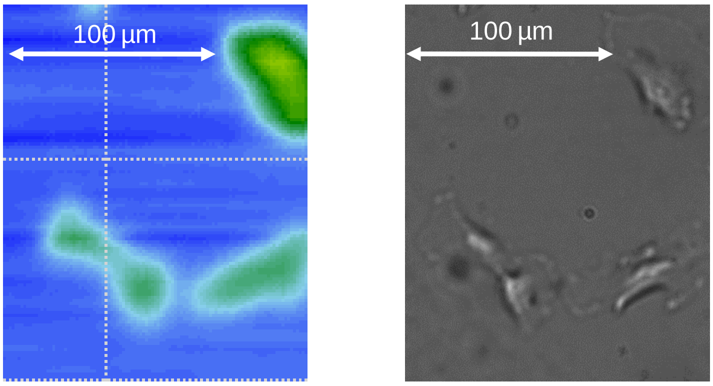
[2] Akos Kriston, Tien Xie, Branko N. Popov, Impact of Ultra-low Platinum loading on Mass Activity and Mass Transport in H_2-Oxygen and H_2-Air PEM Fuel Cells, Electrochimica Acta 121, 116-127 (2014)

Scanning electrochemical microscopy imagery of living tumoral cells at constant height.

Sophie Griveau, Fatemeh Razzaghi, Abdelilah Amar, Johanne Seguin, Fethi Bedioui
PSL Research University, Chimie ParisTech, Unité de Technologies Chimiques et Biologiques pour la Santé
INSERM, Unité de Technologies Chimiques et Biologiques pour la Santé (n° 1022)
CNRS, Unité de Technologies Chimiques et Biologiques pour la santé UMR 8258
Université Paris Descartes, Sorbonne Paris Cité, Unité de Technologies Chimiques et Biologiques pour la Santé
11 Rue Pierre et Marie Curie, 75231 PARIS cedex 05, FRANCE
Sophie.griveau@chimie-paristech.fr

Scanning ElectroChemical Microscopy (SECM) has emerged as very attractive since few years as analytical methods used to study the topography and the response of biological cells to diverse stimuli due to its non invasive character compared to other scanning probe microscopies such as Atomic Force Microscopy (AFM). In addition, SECM makes possible concomitant electro- and physicochemical measurements. Indeed, in SECM, the sharp ultramicroelectrode probe that travels over the sample to be analyzed can also be used as a sensor of topography and/or of the species released by the sample. One of the difficulty when studying morphological studies in real time by SECM, using classical constant height mode is the low contrast of the obtained images due to the insulating character of both biological the cells and of the underlying substrates. Several approaches have been proposed in the literature to improve SECM imagery of living cells, using elegant but generally complex methodologies such as the control of the distance between the probe and the sample during SECM measurements.

In this work, we propose a technical approach to improve the contrast of SECM imagery obtained in the feedback mode and using a redox mediator inert towards the biological cells that allows electrochemical measurements without the need of Faraday cage. To this aim, a piece of biocompatible transparent conductive substrate (indium tin oxide coated PET) was attached into the bottom of cell culture well over which the cells were cultured. The transparency of the substrate is intended to conduct simultaneous SECM and optical microscopy experiments. An endothelial cell line, EA hy.926 was chosen as a model in this study since this cell line is known to undergo cell morphology changes after stimulation by anti-tumoral agent (combrestatatin A4). The obtained results show that the differences in the conductivity of the substrate and of the biological cells enhance the contrast of SECM image in feedback mode at constant height. The SECM results were used to deduce informations about cells morphologies and were compared to those obtained by optical microsocpy. Preliminary studies were also conducted to monitor the kinetics of cell morphology modification under the influence the anti-tumoral agent.



SECM image **Optical image**

Comparison between SECM and optical images of EA.hy 926 adherent cells

References
A. J. Bard, M. V. Mirkin , Scanning Electrochemical Microscopy, Second Edition, CRC Press, 2012
S. Bergner, P. Vatsyayan, F.-M. Matysik, Analytica Chimica Acta 775 (2013) 1– 13
F. Razzaghi, J. Seguin, A. Amar, S. Griveau, F. Bedioui, Electrochimica Acta, doi:10.1016/j.electacta.2015.01.033

Electronic and Catalytic Properties of Hybrid Polyoxometalates Layer Grafted on Conductive and Semiconductive Substrates

Jean-Marc Noël, Florence Volatron, Vitor Brasiliense, Corentin Rinfray, Sarra Gam-Derouich, Catherine Combellas, Frédéric Kanoufi, Anna Proust
Sorbonne Paris Cité, Univ. Paris Diderot, ITODYS, UMR CNRS 7086,
15 rue J. A. Baif, F-75013 Paris, France.
Jean-marc.noel@univ-paris-diderot.fr

The modification of various surfaces by polyoxometalates (POMs) is interesting for many applications including molecular devices for catalysis or electronic memories.[1,2] Indeed POM display several discrete reversible reduction states accessible in a narrow range of potentials electronic levels which make them suitable for the conception of n types memories or for catalysis. In such a context, it is important to develop a strategy leading to the strong immobilization of monolayers of POMs on substrates.

Thus, a strategy to covalently immobilize a monolayer of POMs onto various substrates is presented here (Figure 1). The principle is similar to that recently published with gold and glassy carbon substrates.[3,4] A grafted POM monolayer was then obtained and characterized by AFM, ellipsometry and XPS techniques. Cyclic voltammetry and scanning electrochemical microscopy (SECM) allowed evidencing the vertical and the lateral electron transfers. On one hand, the SECM measurements suggest that the monolayer displays a good lateral conductivity and also the possibility of charge injection and retention inside the layer. On another hand, the catalytic properties of POM layer have been evaluated by cyclic voltammetry. They appeared to be dependent on the supporting electrolyte that can shift the reduction potential of the POM layer.

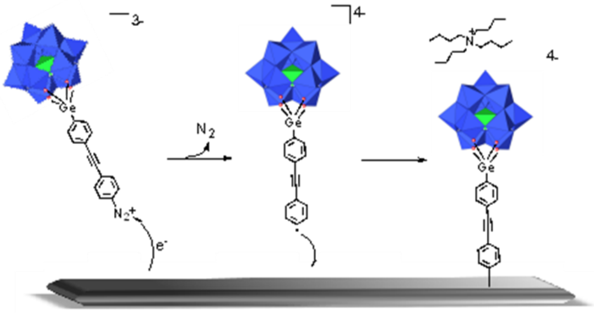


Figure 1: principle of the POM layer grafting on substrates

---

[1] Busche, C.; Vila-Nadal, L.; Yan, J.; Miras, H. N.; Long, D.-L.; Georgiev, V. P.; Asenov, A.; Pedersen, R. H.; Gadegaard, N.; Mirza, M. M.; Paul, D. J.; Poblet, J. M.; Cronin, L. *Nature* **2014**, 515, 545.

[2] Proust, A.; Matt, B.; Villanneau, R.; Guillemot, G.; Gouzerh, P.; Izzet, G. *Chem. Soc. Rev.* **2012**, 41, 7605.

[3] Rinfray, C; Izzet. G., Pinson J., Derouich S.G., Ganem J. Combellas C., Kanoufi, F., Proust A. *Chem. Eur. J.* **2013**, 19, 13838.

[4] Derouich, S. G.; Rinfray, C.; Izzet, G.; Pinson, J.; Gallet, J. J.; Kanoufi, F.; Proust, A.; Combellas, C. *Langmuir* **2014**, *30*, 2287.

Multi-scale simulation of transport processes in metal-oxygen batteries

Timo Danner[*1,2], Birger Horstmann[1,2], Volker P. Schulz[3] and Arnulf Latz[1,2]
[1] *Department of Computational Electrochemistry, Institute of Engineering Thermodynamics, German Aerospace Centre (DLR), Pfaffenwaldring 38-40, 70569 Stuttgart, Germany,*
[2] *Department of Electrochemical Multiphysics Modeling, Helmholtz-Institute Ulm for electrochemical energy storage, Helmholtz-Strasse 11, 89081 Ulm, Germany*
[3] *Baden-Wuerttemberg Cooperative State University, Coblitzallee 1-9, 68163 Mannheim, Germany*

**Presenting author, email: timo.danner@dlr.de, Tel.: +49 (0)711 6862-8218*

Li-Ion batteries are commonly used in mobile electronic devices. However, for some applications, such as electric vehicles (EVs), the energy density is not sufficient [1]. Due to their high theoretical capacity metal-oxygen batteries, e.g. Li-O_2, Zn-O_2, Si-O_2, Mg-O_2, Na-O_2, have the potential to replace Li-ion batteries in next-generation battery powered EVs. In this context systems employing aqueous electrolytes received a renewed interest [2,3]. One of the advantages of aqueous systems is the use of the well-developed concept of gas diffusion electrodes (GDEs) at the cathode. In this kind of electrode a network of hydrophobic binder ensures the coexistence of gas and liquid phase which guarantees a sufficient supply of O_2 from the gas phase even at high discharge rates.

In our contribution we present results bridging the length scales between pore-scale transport and full-cell battery simulations. In a first step 2D and 3D lattice Boltzmann simulations [4,5] are conducted on tomographic reconstructions of Ag model GDEs. The 3D simulations yield information about the distribution of the liquid electrolyte in the porous structure of the GDE. This result can be used to extract effective transport parameters and specific active surface areas at various saturations. Moreover, the simulations are used to obtain p_c-s_w characteristics of the porous media. We demonstrate that computationally less demanding 2D simulations are an efficient tool for the screening of the wetting properties of different new electrode materials and geometries.

The LBM simulations deliver important input parameters for physics-based continuum simulations on the electrode and cell level [2,6]. The continuum models take into account the dissolution, transport and reduction of O_2 in the gas and liquid phase as well as the formation of solid reaction products. A 1D transport model was validated against IV curves and electrochemical impedance spectra recorded in in-house half-cell measurements. We can report excellent agreement between simulation and experiment for various conditions and electrode structures. Finally, the transport model can be inserted at the cathode of virtual metal-O_2 cells for a simulation of discharge characteristics [7].

The multi-scale simulation methodology presented in this work allows predictions of cell performance based on the structural information of the electrode. Therefore, the presented work constitutes an important contribution for a systematic improvement of aqueous metal-O_2 batteries.

REFERENCES

(1) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J.-M. *Nat. Mater.* **2012**, *11*, 19–29.
(2) Danner, T.; Horstmann, B.; Wittmaier, D.; Wagner, N.; Bessler, W. G. *J. Power Sources* **2014**, *264*, 320–332.
(3) Wittmaier, D.; Danner, T.; Wagner, N.; Friedrich, K. A. *J. Appl. Electrochem.* **2013**, *44*, 73–85.
(4) Leclaire, S.; Reggio, M.; Trépanier, J.-Y. *J. Comput. Phys.* **2013**, *246*, 318–342.
(5) Liu, H.; Valocchi, A. J.; Kang, Q. *Phys. Rev. E* **2012**, *85*, 046309.
(6) Horstmann, B.; Danner, T.; Bessler, W. G. *Energy Environ. Sci.* **2013**, *6*, 1299–1314.
(7) Durmus, Y. E.,; Horstmann, B.; Latz, A. Modeling of silicon-air batteries, Ulm, **2013**.

Local characterization by confocal Raman spectroscopy and scanning electrochemical microscopy of liquid/liquid micro-interfaces modified with mesoporous silica

Lukasz Poltorak, Manuel Dossot, Mathieu Etienne, Grégoire Herzog, Alain Walcarius
[1]*LCPME UMR 7564 CNRS – Université de Lorraine,*
405, rue de Vandoeuvre, Nancy, France
Lukasz.poltorak@univ-lorraine.fr

Electrochemical measurements at the **Interface Between two Immiscible Electrolyte Solutions (ITIES)** allow the analytical detection of different classes of ionic species [1], not restricted to electron transfer reactions. ITIES polarization can lead to ion transfer reaction, which makes these sensors unique. Among electroanalytical parameters, its selectivity is still poor and needs to be improved. One of the ways of improvement is the modification of the liquid/liquid interface with a material that possesses selected properties (for instance, sieving). At a solid electrode surface, such property can be obtained with silica materials synthesized by the **Templated Sol-Gel process**. Additionally, under adequate conditions one can control the orientation of the pores and the order quality of mesoporous silica films on electrodes, as it was reported for the electro-assisted self-assembly method [2].

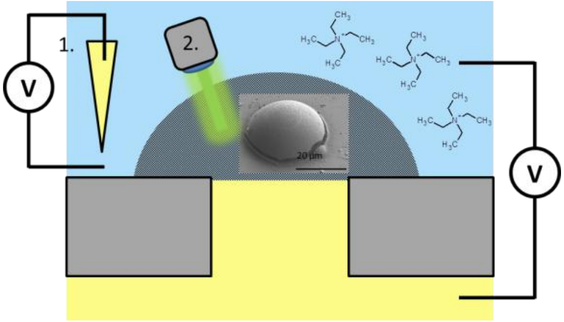


Figure 1. *Schematic representation of a micro-interface modified with mesoporous silica characterized locally by scanning electrochemical microscopy (1) and confocal Raman spectroscopy (2).*

At the liquid/liquid interface, silica film formation involves the presence of a hydrolyzed silica precursor in an aqueous phase, and a template (cationic surfactant) initially dissolved in an organic phase. The Sol-Gel process is triggered by the voltammetric transfer of cationic surfactant from the organic to the aqueous phase, where it catalyses gelation with simultaneous material templating [3].

We will present here how local physico-chemical techniques such as **Confocal Raman Spectroscopy** [4] and **Scanning Electrochemical Microscopy** (equipped with a shear force control [5]) have helped to elucidate the formation mechanism of silica deposits. Confocal Raman Spectroscopy allows the recognition of molecular contribution (organic electrolyte, template molecules) at different stages of deposit formation whereas Scanning Electrochemical Microscopy is employed to evaluate local electrochemical properties of silica supported micro-interfaces.

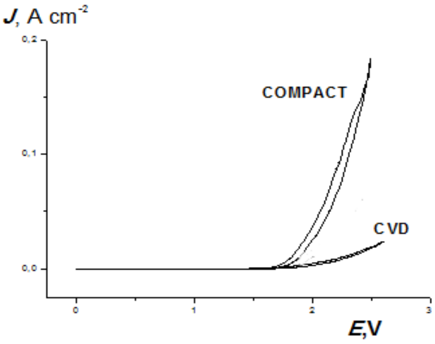
[1] D.W.M. Arrigan, G. Herzog, M.D. Scanlon, J. Strutwolf, in:, A.J. Bard, C.G. Zoski (Eds.), Electroanal. Chem. Vol. 25, CRC Press, Boca Raton, 2013, pp. 105–178.
[2] A. Walcarius, E. Sibottier, M. Etienne, J. Ghanbaja, Nat. Mater. 6 (2007) 602.
[3] L. Poltorak, G. Herzog, A. Walcarius, Langmuir 30 (2014) 11453.
[4] L. Poltorak, M. Dossot, G. Herzog, A. Walcarius, Phys. Chem. Chem. Phys. 16 (2014) 26955.
[5] M. Etienne, S. Lhenry, R. Cornut, C. Lefrou, Electrochim. Acta. 88 (2013) 877.

Electrochemical Behaviour of Boron-doped Diamond Compacts - a New Electrode Material

Yu.V. Pleskov[a], M.D. Krotova[a], V.V. Elkin[a], E.A. Ekimov[b]

[a] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia*
[b] *Institute for High Pressure Physics, 142190 Troitsk, Moscow, Russia*
pleskov@electrochem.msk.ru

Electrochemical properties of a new electrode material, synthetic diamond compacts with the boron (dopant) level approaching the upper limit, are studied for the first time. Cylinder-shaped polycrystalline samples, 3.5-4 mm in diameter and 2.5 mm in height, were prepared by thermobaric processing of graphite-boron carbide mixtures in the diamond thermodynamic stability field (at the pressure of 8-9 GPa and temperature of ~2500 K) [1]. Their diamond nature, in particular, the absence of graphite, was confirmed by Raman spectroscopy and XRD technique. The compacts' electrode behavior is studied by using cyclic voltammetry and electrochemical impedance spectroscopy. The cyclic voltammograms showed that the compacts are similar to conventional chemical-vapor-deposited thin-film diamond electrodes in their electrode characteristics. In particular, they have wide potential window, low background current in indifferent electrolytes (KCl, K_2SO_4) and good reproducibility. Moreover, their extremely high doping level makes them more electroactive (figure) [2].



Thus, the compacts are well comparable to the CVD-diamond electrodes. At the same time, they are free of some drawbacks inherent in the thin-film electrodes (film delamination, thru holes, etc.) One might think that they can equally be used, e.g., as electrodes in electrosynthesis, electroanalysis, water treatment, etc. At the same time their compact form may be an advantage in the designing of electrochemical devices.

[1] E.A. Ekimov, V. Ralchenko, A. Popovich, Diamond Related Mater., 50 (2014) 15–19.
[2] Yu.V. Pleskov, M.D. Krotova, V.V. Elkin, E.A. Ekimov, Elektrokhimiya (in press).

This work was supported by the Russian Foundation for Basic Research, project no. 13-03-00660.

SECM meets electrocatalysis

Wolfgang Schuhmann[1], Justus Masa[1], Daniela Wintrich[1],
Alexander R. Botz[1], Michaela Nebel[2]

Analytische Chemie - Center for Electrochemical Sciences – CES,
Ruhr-Universität Bochum, Universitätsstr. 150, 44780 Bochum, Germany
[2]Sensolytics GmbH, Universitätsstr. 142, D-44799Bochum, Germany
wolfgang.schuhmann@rub.de

The increasing demand of using sustainable energy supplies substantially increases the need for the development of novel highly active electrocatalysts for the conversion of discontinuously obtained solar or wind energy into chemical bonds.

For the evaluation of catalyst materials the determination of the onset potential of the gas evolution reaction, catalyst stability, gas bubble departure, catalyst conductivity and behavior at high current densities at minimal catalyst loading are of high importance. Moreover, the catalyst powder is often immobilized at an electrode surface using a binder such as Nafion, which may influence the catalytic activity of the material.

The following topics will be discussed:

1. SECM and rotating ring-disk electrodes: Complementary insights into catalyst activity and selectivity
2. recessed Au microelectrodes and dual-barrel recessed Au microelectrodes for binder-free catalyst immobilization
3. shearforce-based positioning of Pt nanoelectrodes above catalyst-filled cavity electrodes and determination of the onset potential of oxygen evolution

Acknowledgement: Financial support from the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft and in the framework of the Helmholtz-Energie-Allianz "Stationäre elektrochemische Speicher und Wandler" (HA-E-0002) is gratefully acknowledged.

Unprecedented Efficiency to Simultaneously Control Orbital Energies and Vibrational Properties of Single-Molecule Junctions in Eectrochemical Environment

Ioan Bâldea
Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany
Phone: +49-6221-545214, Fax: +49-6221-545221
ioan.baldea@pci.uni-heidelberg.de

The present paper reports on recent and ongoing work on the control of single (redox) molecules embedded in scanning tunneling microscope (STM) junctions in electrochemical (EC) environment.

As we shown recently [1], the electrochemical setup provides a unique chance to control the molecular orbital energies and vibrational properties. The key role in the unprecedented efficiency of this control is played by the electrolyte gating, which enables a continuous change in the molecular charge by up to an entire electron (complete redox process). The redox unit (viologen) considered in ref. 1 is based on 4,4'-bipyridine (44BPY), a molecule of special interest for the charge transport at nanoscale, on which we focused in a series of recent studies.[2,3,4,5]. An aspect emphasized in ref. 1 is that changes in the surface enhanced Raman spectrum (SERS) due to molecular charge changes are substantial and robust against strong stochastic fluctuations inherent in molecular junctions [6].

For SERS observability, the electromagnetic enhancement near a sharp metallic STM tip is essential, but sometimes this enhancement alone does not suffice; supplementary (*e.g.* chemical) enhancement factors are desirable. In this vein, we will present examples demonstrating that the solvent can have a significant and nontrivial impact on the SERS intensity. The preliminary results presented in Fig. 1 may serve as illustration.

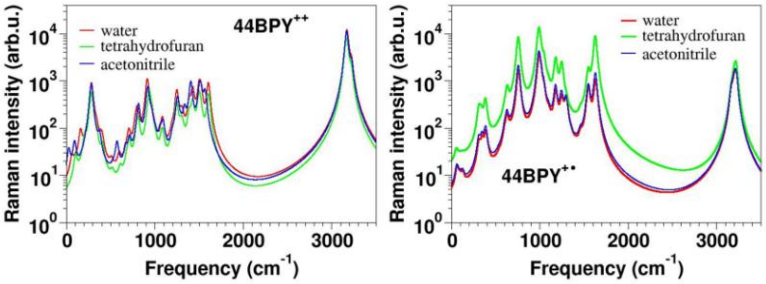


Fig. 1 Raman spectra of the dicationic and cationic species in different solvents (indicated in the legend) exhibit substantial differences. Notice the logarithmic scale on the ordinate axis, chosen to demonstrate the nontrivial solvent impact, which does not merely reduce to a multiplicative factor.

In addition to SERS, results of ongoing work on surface enhanced infrared absorption (SEIRA) for the aforementioned EC-STM junctions will also be reported.

---

[1] I. Bâldea, Electrochemical setup – a unique chance to simultaneously control orbital energies and vibrational properties of single-molecule junctions with unprecedented efficiency, Phys. Chem. Chem. Phys.16 (2014) 25942.

[2] I. Bâldea, Transition voltage spectroscopy reveals significant solvent effects on molecular transport and settles an important issue in bipyridine-based junctions, Nanoscale 5 (2013) 9222.

[3] I. Bâldea, A quantum chemical study from a molecular transport perspective: ionization and electron attachment energies for species often used to fabricate single-molecule junctions, Faraday Disc. 174 (2014) 35.

[4] I. Bâldea, H. Köppel and W. Wenzel, (4,4')-Bipiridine in vacuo and in solvents: A quantum chemical study of a prototypical floppy molecule from a molecular transport persoective, Phys. Chem. Chem. Phys. 15 (2013) 1918.

[5] I. Bâldea, Demonstrating why DFT-calculations for molecular transport in solvents need scissor corrections, Electrochem. Commun. 36 (2013) 19.

[6] I. Bâldea, Interpretation of stochastic events in single-molecule measurements of conductance and transition voltage spectroscopy, J. Am. Chem. Soc. 134 (2012) 7958.

PEDOT Electrochemical Sensors using Macro and Micro-Electrodes

P.A. Kilmartin[1], A. Türke[2], H. Karaosmanoglu[1], Q. Zhang[1]
[1] School of Chemical Sciences, University of Auckland, Auckland, New Zealand.
p.kilmartin@auckland.ac.nz
[2] ILK Dresden gGmbH, Bertolt-Brecht-Allee 20, 01309 Dresden, Germany

The polymer PEDOT (poly(3,4-ethylenedioxythiophene)) is a conductive electrode material that is being considered for a number of technological applications. One property of interest is the excellent sensing capabilities exhibited by PEDOT as a sensor for oxidisable analytes [1]. Electropolymerization has been performed with 0.1 M 3,4-ethylenedioxythiophene (EDOT) and 0.1 M lithium perchlorate in propylene carbonate using cyclic voltammetry at 1 to 3 mm diameter glassy carbon and gold electrodes [2]. The thickness of the resulting PEDOT layer has been controlled through the number of preparative cycles, after which the PEDOT sensors have been tested in solutions containing polyphenols and other small molecule antioxidants, and in beverage samples.

Excellent separation of signals due to ascorbic acid and sulfites, alongside the response due to the oxidation of polyphenols in beverages, has been achieved using the redox-mediating properties of PEDOT [1]. An approach to measuring these wine antioxidant additives in the presence of beverage polyphenols has thus been demonstrated. Comparisons have been made between the voltammograms obtained for polyphenols such as caffeic acid, catechin and epigallocatechin gallate, representing prominent tea and wine polyphenols, at both PEDOT and glassy carbon electrodes [2]. A higher current response has been obtained at the PEDOT electrodes with evidence for the build-up of adsorbed polyphenols occuring at the PEDOT electrodes. The enhanced sensitive has transferred to the analysis of green tea and wine samples with PEDOT electrodes, with the added advantage that beverages do not need to be diluted to the extent required for reliable measurement at glassy carbon electrodes. Good correlations have been obtained for a wide number of beverages with conventional assays for beverage antioxidant activity.

When PEDOT is electropolymerised at 10 µm sized microelectrodes in certain electrolytes, growth is not limited to the sub-micrometer sized particles or dense film layers typical of most conducting polymers, but an extensive fractal-type growth is seen (Figure 1). These highly nanostructured sensors are being considered for use in micro-electrode arrays for multiple target analytes. Currents due to oxidation of analytes at the PEDOT microelectrodes have been found to increase by up to 50-fold, and represent an electrode morphology for conducting polymers comparable to high surface area platinised platinum for inert metal electrochemistry.

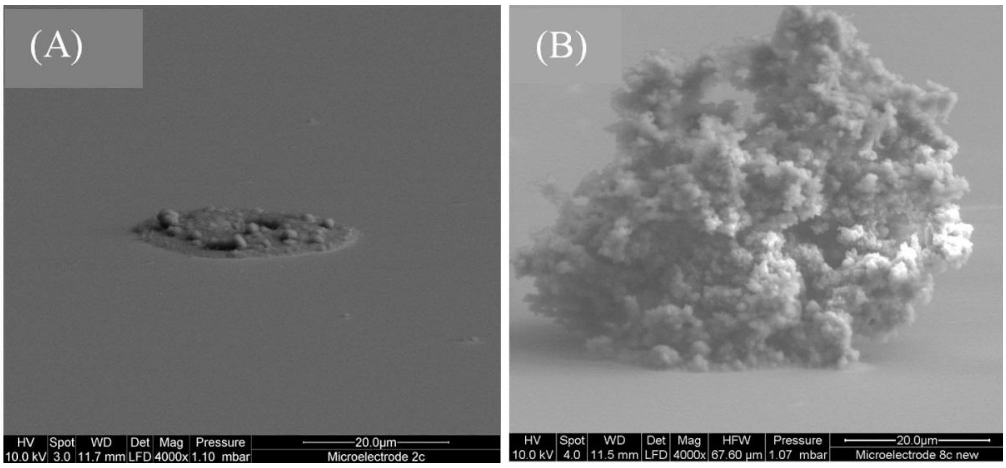


Figure 1. SEM images of PEDOT growth on a 10 µm gold electrode, after (A) two, and (B) eight preparative cycles (5 minutes of electropolymerisation).

[1] A. Türke, W.-J. Fischer, N. Beaumont, P.A. Kilmartin, Electrochim. Acta **60**, 184 (2012)
[2] H. Karaosmanoglu, J. Travas-Sejdic, P.A. Kilmartin, Int. J. Nanotechnol. **11,** 445 (2014)

Electrochemical Sizing and Detection of Magnetic Field-Induced Agglomeration of Individual Fe_3O_4 Nanoparticles

Kristina Tschulik, Richard G. Compton
Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK
Tschulik.Kristina@gmail.com

Magnetite nanoparticles (Fe_3O_4 NPs) have widespread application in magnetic field based medical treatments– both in well-established techniques, such as MRI scanning for diagnostics and in therapeutical methods of the future such as hyperthermia or targeted drug delivery. Hence, measuring the subsequent distribution of magnetic nanoparticles in the human body and identifying the effects of the applied magnetic fields on nanoparticle agglomeration and biodegradation are very challenging, yet important, analytical tasks.

Here we present Anodic (APC) and Cathodic Particle Coulometry (CPC) as electrochemical methodologies to solve these tasks, as they allow for detecting and sizing individual magnetite nanoparticles in a solution and in the presence or the absence of magnetic fields. Particle Coulometry measures the charge transferred when a particle impacts an electrode that is held at a potential sufficient to either reduce (CPC) or oxidize (APC) this particle (Fig. 1). Using Faraday's law the charge transferred per impact provides the number of redox-active species in each nanoparticle and thus individual particle sizes and agglomeration states can be determined [1]. For mixed oxides like Fe_3O_4 both APC and CPC can be applied complementarily to intrinsically validate the experimental results [2]. While the used superparamagnetic Fe_3O_4 nanoparticles were found to be stable against agglomeration even in the presence of electrolytes of high ionic strength (0.2 M phosphate buffer), the application of a magnetic field of 0.3 T caused individual nanoparticles to agglomerate to larger clusters in the same solution [3]. Moreover, the dissolution of Fe_3O_4 was found to be strongly retarded in the presence of the magnetic field, an effect that is attributed to the action of the strong magnetic field gradient force at the nanoparticle surface.

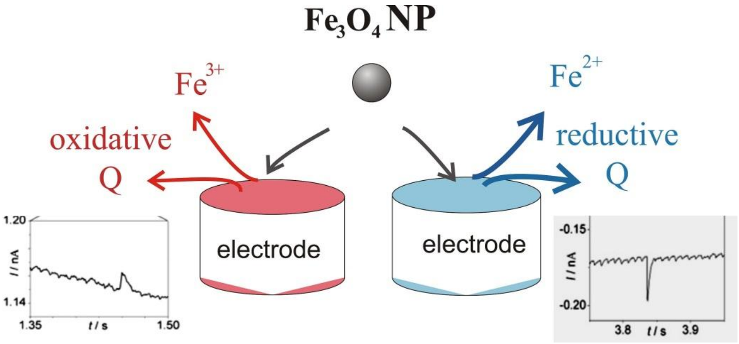


Fig. 1: Schematic drawing showing the principle of nanoparticle impact based sizing of individual magnetite nanoparticles via Anodic (left) and Cathodic Particle Coulometry (right).

References:

[1] Y.-G. Zhou, N.V. Rees, R.G. Compton, *The Electrochemical Detection and Characterization of Silver Nanoparticles in Aqueous Solution*, Angew. Chem. Int. Ed. 50 (2011) 4219–4221.

[2] K. Tschulik, B. Haddou, D. Omanović, N.V. Rees, R.G. Compton, *Coulometric sizing of nanoparticles: Cathodic and anodic impact experiments open two independent routes to electrochemical sizing of Fe_3O_4 nanoparticles*, Nano Res. 6 (2013) 836–841.

[3] K. Tschulik, R.G. Compton, *Nanoparticle impacts reveal magnetic field induced agglomeration and reduced dissolution rates*, Phys. Chem. Chem. Phys. 16 (2014) 13909–13913.

Novel glucose sensor based on electrocatalytic reduction of hydrogen peroxide at Au@Ag heterogeneous nanorods

Aihua Liu*, Shu Zhang and Lei Han □
Laboratory for Biosensing, Qingdao Institute of Bioenergy &
Bioprocess Technology, Chinese Academy of Sciences
189 Songling Rd, Qingdao 266101, China
liuah@qibebt.ac.cn

Noble metal nanomaterials were found to have catalytic activity towards H_2O_2 reduction due to their high effective surface areas, size controlled electrical properties and excellent stability. To date, pure gold nanoparticles and sliver nanoparticles have been reported to be good electrocatalyst for H_2O_2. However, they still have some disadvantages, such as exhibiting activity only at alkaline pH condition and experiencing serious poison in the presence of excess Cl^-.

Considering the biocompatibility of gold and excellent catalytic activity of sliver, the Au@Ag heterogeneous nanorods (Au@Ag NRs) were synthsized. The Au@Ag NRs exhibited favorable electrocatalytic ability to reduce H_2O_2 at negative potential of about -0.6 V (vs. SCE). Further, the glucose-oxidase/Au@Ag NRs modified electrode was constructed as glucose sensor, which exhibited wide linear range of 0.02−10 mM glucose in O_2-saturated phosphate buffered solution at an applied potential of -0.4 V. The glucose sensor showed a good reproducibility, stability and selectivity for possible interferents (such as ascorbic acid, uric acid and dopamine), some other saccharides and 0.15 M chloride ions. Considering the neutral pH condition and good sensing performance, the proposed sensor could be further used in practical analysis.

References

[1]. L. Han, D.P. Yang, A. Liu, *Biosens. Bioelectron.* **2015**, *63*, 145-152.
[2]. L. Han, S. Zhang, L. Han, D.P. Yang, C. Hou, A. Liu, *Electrochim. Acta* **2014**, *138*, 109-114.
[3]. X. Jia, G. Hu, F. Nitze, H. R. Barzegar, T. Sharifi, C.-W. Tai, T. Wågberg, *ACS Applied Materials & Interfaces* **2013**, *5*, 12017-12022.

Agglomerate Catalyst Layer Model on the Membrane Electrode Assembly of Proton Exchange Membrane Fuel Cell

Ken-Ming Yin*, Yu-An Kung, Bo-Syun Cheng
Department of Chemical Engineering and Materials Science
135 Yuan Tung Road, Chung Li, Taoyuan, Taiwan 32003
**cekenyin@saturn.yzu.edu.tw*

Many researchers treated the catalyst layer as a reactive plane without thickness in the modeling of proton exchange membrane fuel cells (PEMFCs). This is a simplified approach without the complication of finite region of coupled mass transfer and electrochemical reaction. However, evaluation of the various fabrication techniques of membrane electrode assembly (MEA) in laboratories cannot be guided by such models. Here, finite catalyst layer is assembled by many agglomerates of secondary particles that are composed of carbon supported platinum nano-particles and dispersed solid polymer electrolytes. The void space between agglomerates is filled with water vapor, reactant gases, as well as flooded liquid water. Fig. 1 is a schematic of the cathode compartment of MEA. The performance of PEMFC depends on the gas and water transport in the gas diffusion layer, the state of hydration in the membrane, and most important, the mass transfer and electrochemical reaction within the catalyst layer.

In the agglomerate catalyst layer model, gas transport in gas diffusion layer and catalyst layer is described by the Stefan-Maxwell equations. Liquid water transfer in these two layers is driven by the capillary force gradient. Liquid water in the membrane phase is transferred by the electro-osmotic drag. Note the geometric structure of the catalyst layer is specifically considered. The thickness of the catalyst layer is about 10 μm, the agglomerate is about 1 μm, the carbon particle diameter is about 10-100nm, while the platinum catalyst particle adsorbed on the carbon is about 2-5nm. The operating parameters studied in the model include inlet degree of humidification, cell temperature, and the pressure drop between anode and cathode.

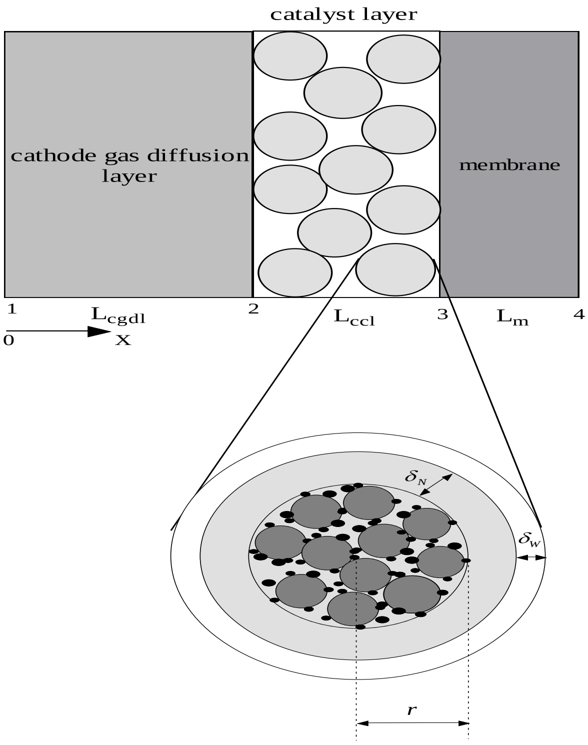


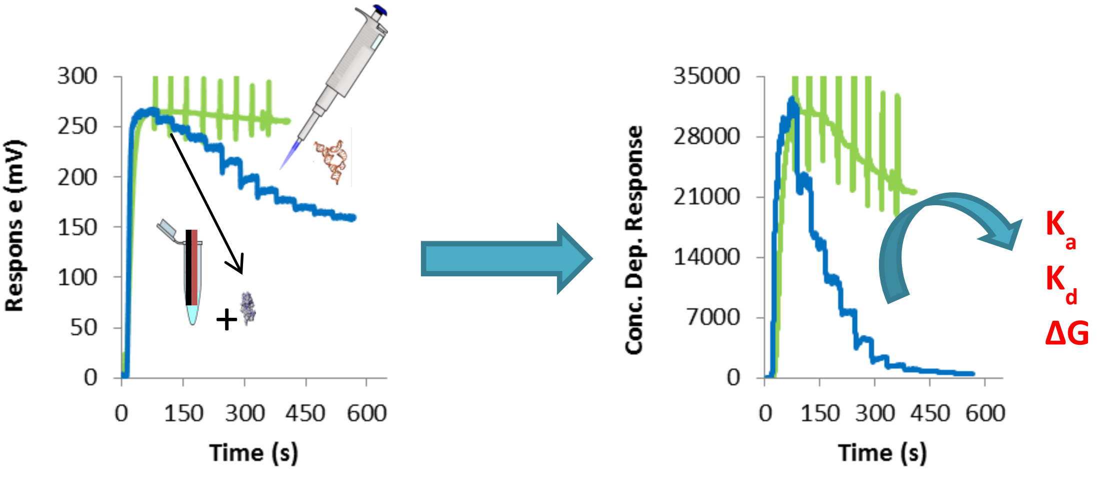
Fig..1 Schematic of the modeling domain (not to scale).

Determination of the Association Constant Between Small Target Molecules and Large Biomolecules by Potentiometric Titration

Ezat Hamidi-Asl[1] , Luc J. Nagels[2], Devin Daems [2,3], Guy Van Camp[3], Karolien De Wael[1]

[1]*AXES research group, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium*
[2]*Chromatographic Organic Trace Analysis, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium*
[3]*Centre of Medical Genetics, Department of Biomedical Sciences, University of Antwerp, Universiteitsplein 1, 2610 Antwerp, Belgium*
Ezat.Hamidi-Asl@uantwerpen.be; luc.nagels@uantwerpen.be; devin.daems@biw.kuleuven.be; guy.vancamp@uantwerpen.be; karolien.dewael@uantwerpen.be

In the present article, the utility of a potentiometric titration approach for recognition and calculation of biomolecule/small molecule interactions is reported. This approach is fast, sensitive, reproducible and inexpensive in comparison to the other methods for the determination of association constant values (K_a) and interaction energies (ΔG). The potentiometric titration measurement is based on the use of a classical polymeric membrane indicator electrode in a solution of the small molecule ligand. The biomolecule is used as a titrant. The potential is measured versus a reference electrode and transformed to a concentration related signal over the entire concentration interval, also at low concentrations, where the mV (y-axis) versus $\log c_{analyte}$ (x-axis) potentiometric calibration curve is not linear. In the procedure, the K_a is calculated for the interaction of cocaine with a cocaine binding aptamer and with an anti-cocaine antibody. To study the selectivity and cross-reactivity, other oligonucleotides are tested, as well as other small ligand molecules such as tetrakis (4-chlorophenyl)borate, metergoline, lidocaine, and bromhexine. The calculated K_a compared favorably to the value reported in the literature using SPR. The newly presented potentiometric titration approach (called "Concentration related Response Potentiometry"), makes it possible to study molecular interaction for a variety of macromolecular target molecules and small molecule ligands [1]



Reference:
[1] E. Hamidi-Asl, D. Daems, K. De Wael, G. Van Camp, L.J. Nagels; Anal. Chem., Article ASAP, DOI: 10.1021/ac503385x

Influence of local lithium metal deposition in 3D microstructures on local and global behavior of Lithium-ion batteries

Simon Hein[1,2,3], Arnulf Latz[1,2,3]
[1] Department of Computational Electrochemistry, Institute of Engineering Thermodynamics, German Aerospace Centre (DLR), Pfaffenwaldring 38-40, 70569 Stuttgart, Germany,
[2] Helmholtz-Institute Ulm for Electrochemical Energy Storage, Helmholtz-Strasse 11, 89081 Ulm, Germany
[3] Institute of Electrochemistry, University Ulm, Albert-Einstein-Allee 11, 89069 Ulm, Germany
Email: Simon.Hein@dlr.de, Tel.: +49 731 5034 307

Lithium-ion batteries are used in nearly all electronic devices, be it consumer electronics or mobile electrical vehicles. Especially for electromobility applications it is vitally important, that the batteries can be operated safely and reliably under various operation conditions. A very critical degradation mechanism is Lithium plating. It becomes dominant under high applied current densities especially at low temperatures. A better understanding how microstructural features of the anode can influence where exactly and when lithium plating takes place is crucial in designing structured electrodes, which minimize the probability of Lithium plating. Even if locally Lithium is already deposited, it is important to understand, how the presence of metallic Lithium films modifies the local conditions in the anode and the global behavior of the cell, in order to develop ideas for providing more detailed input for battery management systems.

To approach this goal we extended our existing 3D microstructure resolved modeling and simulation technology [1, 2] for Lithium Ion batteries to the simulation of cells in which lithium plating is present. The model is developed on two scales. On the microstructural, pore resolved scale Lithium metal is simulated as a third phase in addition to electrolyte and active particles. On the scale of the SEI an effective interface model is derived, which captures the initiation of plating by modeling transport and reactions in the solid and electrolyte part of the SEI.

To gain insight, how plated lithium influences the performance and electrochemical conditions inside the 3D microstructure of a lithium-ion battery, 3D microstructure resolved electrochemical simulations of Li ion battery cells are performed. From these simulations we obtain information on where locally the necessary conditions for plating are fulfilled. In addition we investigate how the local electrochemical conditions are modified by the presence of a lithium film, dependent on the position and amount of plated Lithium.

As a second step an effective interface model is developed which describes lithium plating and its interplay with SEI growth. This model is based on the formulation of explicit interface conditions for the four involved phases (electrolyte, anode material, solid part of SEI and Lithium). Fig. 1 sketches the four different phases. In order to allow the integration of these interface conditions in the fully 3D microstructure resolved simulation tool, possible simplifications of the full interface model are investigated. With these effective interface conditions, the feedback of local Lithium plating events on the operation of the whole cell will be possible.

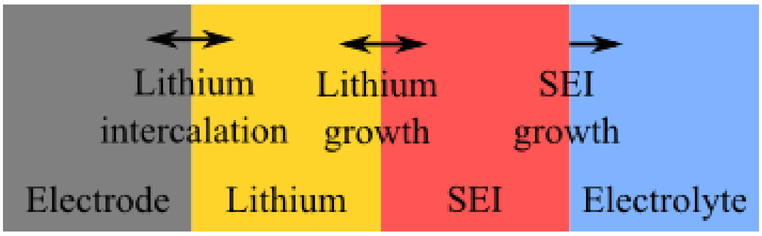


Figure 1: Sketch of the four phases used for the modelling of the effective interface condition

[1] Battery and Electrochemical Simulation Tool, http://www.itwm.fraunhofer.de/best
[2] A. Latz and J. Zausch, J. Power Sources, 196 (2011), pp. 3296–3302.

Electrochemical, PMIRRAS, and ATR-IR Characterization of a New Bacteriocin-like Antimicrobial Peptide at a Model Biological Membrane

Piotr Pieta[1], ZhangFei Su[2], Michael Grossutti[3], Pawel Mak[4], Benedykt Wladyka[4], Jacek Lipkowski[2]

[1]Institute of Physical Chemistry Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warsaw, Poland
[2]Department of Chemistry and [3]Department of Physics, University of Guelph
50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada
[4]Department od Analytical Biochemistry, Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University
Gronostajowa 7 St., 30-387 Krakow, POLAND

e-mail address: ppieta@ichf.edu.pl

A phospholipid bilayer with a new bacteriocin-like antimicrobial peptide was deposited on an Au(111) electrode surface. Polarization modulation infrared reflection absorption spectroscopy (PMIRRAS) and polarized attenuated total reflection infrared (ATR-IR) spectroscopy measurements were used to characterize structural and orientational changes in this model biological membrane upon binding the peptide and the application of the electrode potential. The data show that binding the peptide to the membrane did not change the tilt angle of the fatty acid chains of phospholipids; however, changes in the applied potential had significant effect on the peptide structure and the membrane conformation. Both PMIRRAS and ATR-IR were utilized to determine the tilt angle of the alpha-helical part of the peptide adsorbed on the model membrane.

References:

1. M. Grossutti, R.Seenath, S. Conlon, J. J. Leitch, J. Li, J. Lipkowski, *Langmuir*, **2014**, 30 (36), 10862.
2. J. J. Leitch, C. L. Brosseau, S. G. Roscoe, K. Bessonov, J. R. Dutcher, J. Lipkowski, *Langmuir*, **2013**, 29 (3), 965.

Immobilization of dehydrogenases on macroporous carbon felt by click chemistry for electroenzymatic synthesis

Lin Zhang,[1] Mathieu Etienne,[1] Ievgen Mazurenko,[1] Gert W. Kohring,[2] Neus Vilà,[1] Alain Walcarius[1]

[1] *LCPME UMR 7564 CNRS – Université de Lorraine,*
405, rue de Vandoeuvre, Nancy, France
[2] *Microbiology, Saarland University, Campus, Geb. A1.5, D-66123 Saarbruecken, Germany*

l.zhang@univ-lorraine.fr

Compared to conventional organic synthesis, enzymatic electrosynthesis is a green and sustainable processes suitable for the multi-step reactions under mild conditions with higher yields. During the process, the key step to successful electrosynthesis is enzyme immobilization. Up to now, different strategies for immobilization of enzymes on porous materials has been developed in order to enhance the stability as well as catalytic activity and the recyclability of the enzymes [1].

In the present work, a facile metal-free ‘click’ type thiol-ene reaction [2] was utilized to immobilize D-sorbitol dehydrogenase (DSDH) on carbon felt (CF). This bio-system is proved to be stable and efficient for enzymatic oxidation of D-Sorbitol, and the direct electrochemical regeneration of NADH has been successfully applied. Besides, the multi-wall carbon nanotube was deposited on the carbon felt in order to increase the surface area and efficiency of this DSDH-CNT/CF system. Meanwhile, DSDH catalyzed enzymatic reduction of D-Fructose with electrochemical NAD^+ regeneration was realized by using $[Cp^*Rh(bpy)Cl]^+$ mediator in the solution, which is promising in electroenzymatic synthesis.

[1] M. Hartmann, D. Jung, Biocatalysis with enzymes immobilized on mesoporous hosts: the status quo and future trends, J. Mater. Chem. 20 (2010) 844.

[2] M.W. Jones, G. Mantovani, S.M. Ryan, X. Wang, D.J. Brayden, D.M. Haddleton, Phosphine-mediated one-pot thiol-ene “click” approach to polymer-protein conjugates, Chem. Commun. (2009) 5272.

Structural and Electrochemical Study of a coated stainless steel 304L by PVD method

L. BAIT [1,2,] *, N. MADAOUI [1,2], N. SAOULA [1]

[1]*Division Milieux Ionisés, Centre de Développement des Technologies Avancées*
CDTA Cité du 20 août 1956, Baba Hassen, BP n°17, Alger, Algérie
[2]*Laboratoire d'Electrochimie-Corrosion, Métallurgie et Chimie Minérale. Faculté de Chimie.*
Université Des Sciences et de la Technologie Houari Boumediene. B.P 32, El Alia, Bab Ezzouar, Alger 16111,
*E-mail: lbait@cdta.dz

Abstract:

In this work, we studied the corrosion resistance of 316l and 304l in a physiological medium containing salts on one side, and on the other hand, we made a deposit by magnetron sputtering method on the same steel and that for better corrosion resistance. Electrochemical methods are the potential drop, polarization curves and impedance measurements and characterization techniques accompany these analysis methods.

This study has been realized based on different techniques such as magnetron sputtering (PVD techniques) and other characterization techniques including optical microscopy and SEM (Scanning Electron Microscopy) coupled to the EDS, XRD, microhardness and corrosion tests performed by an electrochemical cell controlled by a software studio 4 versa.

Key words: 304l, 316l, PVD, Electrochemical study, Stainless steel.

Protection of stainless steel for corrosion application by titanium dioxide PVD coating in 3.5% NaCl solution.

N. Madaoui [1,2,*], N. Saoula [1], K. Kheyar [1], A. Hammouche [1], S. Nezar [1], S. Belhousse [3], C. Yaddaden [3].

[1] *Division Milieux Ionisés, Centre de Développement des Technologies Avancées*
CDTA Cité du 20 août 1956, Baba Hassen, BP n°17, Alger, Algérie
[2] *Laboratoire d'Electrochimie-Corrosion, Métallurgie et Chimie Minérale. Faculté de Chimie. Université Des Sciences et de la Technologie Houari Boumediene. B.P 32, El Alia, Bab Ezzouar, Alger 16111, Algérie.*
[3] *Centre de Recherche en Technologie des Semi-conducteurs pour l'Energétique CRTSE - 02, Bd. Dr. Frantz FANON, B.P. 140 Alger-7 Merveilles 16038, Algérie.*

**E-mail : nmadaoui@cdta.dz*

Abstract: In this work, we investigate the effect of TiO_2 coatings on the microstructure, hardness and corrosion behavior. A series of TiO_2 coatings was deposited onto stainless steel substrates without intentional heating or biasing by magnetron sputtering (13.56 MHz) of a titanium target using Ar/O_2 reactive mixtures over a broad range of total sputtering pressures for 15 and 30 mTorr. Their microstructure and hardness were investigated using XRD, MEB and nanoindentation. Electrochemical corrosion behavior of the coated stainless steel substrates was evaluated in simulated marine environment in 3.5 wt.% aqueous NaCl solution by potentiodynamic polarization. Corrosion potentials (Ecorr) and the corrosion current densities (icorr) were calculated by using instantaneous Tafel-type fit Versa Studio corrosion analysis software.

Keywords: TiO_2, Corrosion behavior, Stainless steel, coatings, magnetron sputtering.

Amperometric Quantitative Measurements of Individual Vesicular Contents in Single Cells

Xianchan Li[1,2*], Soodabeh Majdi[2], and Andrew G. Ewing[1,2]
[1] *Department of Chemistry and Molecular Biology, University of Gothenburg, , Kemivägen 10, SE-41296 Gothenburg, Sweden,* [2] *Department of Chemical and Biological Engineering, Chalmers University of Technology, Kemivägen 10, SE-41296, Göteborg, Sweden*
xianchan@chalmers.se

Neurons communicate via the processes of releasing and taking in chemical messengers. These neurotransmitters are packaged in nanometer-size synaptic vesicles located in the cell. Quantification of vesicular transmitter content is important in order to study mechanisms of neurotransmission and malfunction in disease and yet this it is incredibly difficult to measure these small quantities in the attoliter volume of a single vesicle. We describe our progress on a new approach, electrochemical cytometry, to carry out measurements of the total amount of catecholamine transmitters present in individual synaptic vesicles in single cells. We have applied this method to measure the content of vesicles from PC12 cells and have shown the levels in a single dense core vesicle to range from a few thousand to millions of molecules. In addition, these levels can be changed with pharmacological manipulation indicating a new mechanism for discovery of neuroactive drug candidates.

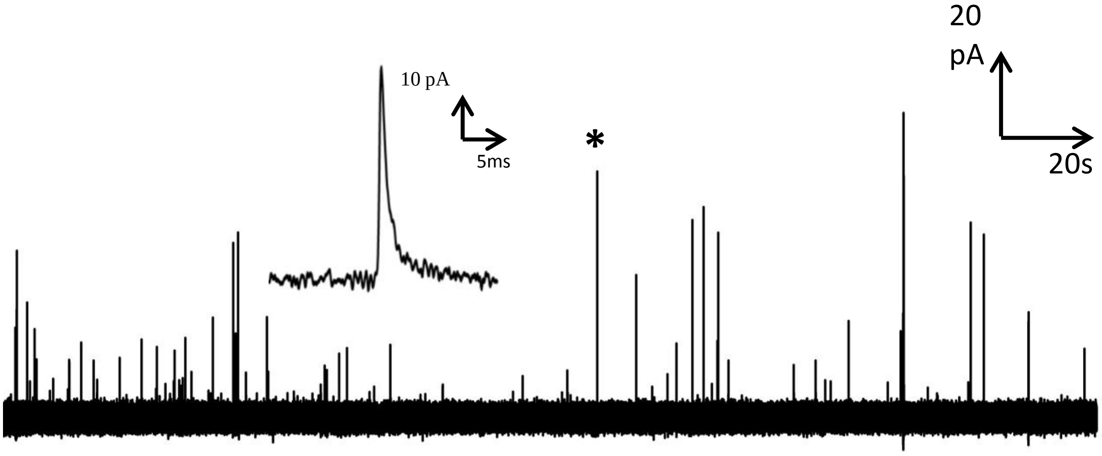


Figure 1. Representative amperometry of a nano-tip conical CFME inside a PC12 cell. Inset: An amplified example of an amperometric current trace.

Hydrogen Production from Water Electrolysis for the storage of offshore wind energy

Philippe Mandin[1], Yann Le Guennec[1], Envel Guezennec[2], Alexandre Solacolu[2], Pascal Morançais[1]

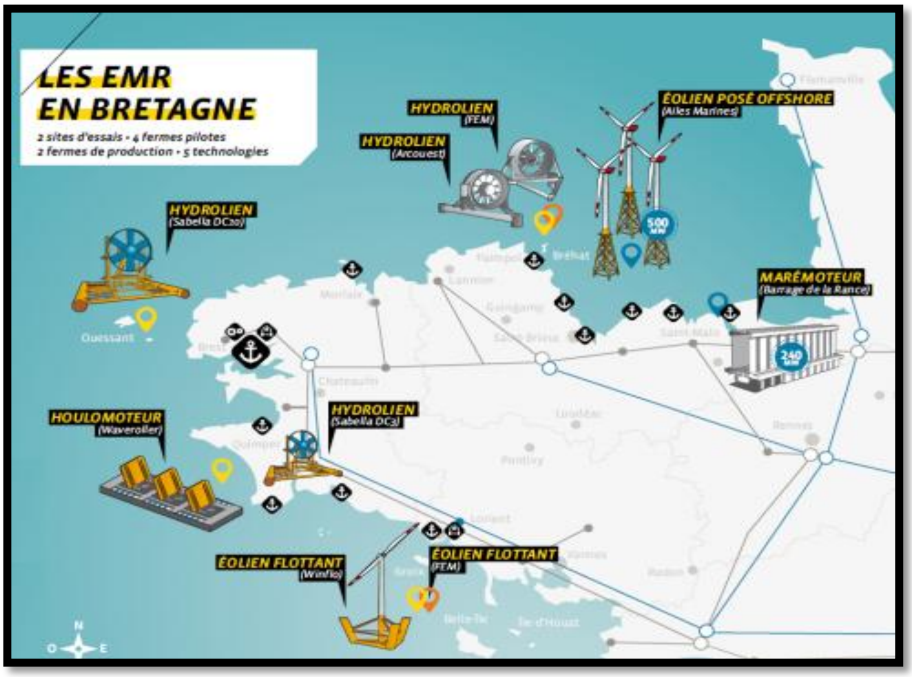
[1]*Université de Bretagne Sud,*
Laboratoire d'Ingénierie des Matériaux de Bretagne
Centre de Recherche, rue de Saint-Maudé,
56100 Lorient, FRANCE
[2]*Saint-Brieuc Agglomération, France*

Abstract

Over the last few years, public awareness on energy efficiency and global warming does pressure on governments to adopt urgent and efficient solutions. In this context, hydrogen can impose oneself as a key element of a sustainable energy model. To be really sustainable, hydrogen has to be produced from renewable energy, for example, wind energy.

In this respect, the Saint-Brieuc project's of offshore wind turbines can be a good opportunity to develop hydrogen production. First of all, it can be interesting to ask some questions, why storage? Why hydrogen? After answering these questions, it is necessary to find local applications for hydrogen in order to increase the regional attractiveness. The hydrogen will be generates by water electrolysis, which use electricity of wind farm. This one will be composed of 62 wind turbines, with a power of 5 MW each for a production estimate of 1 850 GWh per year. On the other hand, the water electrolysis produce heat and oxygen, for a better energy model it's important to increase the status of this components.

During two-phase electrolysis processes, in this case for hydrogen production, there are bubbles which are created at electrodes. This implies a great vertical motion source in the normal earth gravity field and then a quite important natural two-phase convection. All other fields are then affected. Heat, mass and electricity transfers are modified due to both bubbles screening (at surface and in volume) and to bubbles transport promotion. These fields as overvoltage can be studied when there is a fluctuating electric source to take into account intermittency of the wind energy. Many numerical modeling for two-phase processes. In boiling or electrolysis processes, a difficulty is added: particles birth or injection is strongly coupled to the local flow properties and leads to a complex boundary condition at surfaces. Electrical and electrochemical properties and processes are disturbed. This disturbance can lead to the modification of the local current density and to anode effects for example.



Key words: Two-phase electrolysis, hydrodynamic electrochemical processes

Electrodeposition of nickel using eutectic mixtures based in ionic liquid formulations

Paula M. V. Fernandes, Carlos M. Pereira*, A. Fernando Silva
CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências,
Universidade do Porto, 4169-007 Porto, Portugal
**cmpereir@fc.up.pt*

From the industrial and technological perspective Nickel is still an important metal in coatings for corrosion protections electrocatalysis and magnetic properties and batteries [1, 2]. The electrodeposition of Nickel has been widely practiced in aqueous plating systems [3,4]. However, the hydrogen evolution reaction that occurs during electrodeposition has a profound effect on current efficiency and the final quality of Nickel deposits. Problems associated with hydrogen evolution can in principle be avoided by employing ionic liquids as they can be made water free [5]. In the recent years the metal deposition from ionic liquids is an area which attracted much attention due to the possibility of depositing metal which cannot be otherwise deposited and for the possibility to replace the toxic baths used commercially [6]. One particular type of ionic liquids is called Deep Eutectic Solvent (DES) and is based on a mixture of choline chloride with suitable hydrogen bond donors [6].

This communication presents the electrodeposition of Nickel using a eutectic mixture based ionic liquids. The electrochemical profile of nickel was studied by cyclic voltammetry and the nucleation/growth process was investigated using chronoamperometry. The resultant surface of Nickel morphology was revealed by SEM.

Acknowledgments: This work was supported by the NanoCoatIL project contract number M-ERA.NET/0009/2012.

[1] A. P. Abbott, G. Capper, B. Swain and D. Wheeler: Trans. IMF 82 (2005) 51–54.
[2] A. P. Abbott, G. Capper, K. J. McKenzie and K. S. Ryder Electrochim. Acta 51 (2006) 4420.
[3] G.Z. Meng, F.L. Sun, Y.W. Shao, T. Zhang, F.H. Wang, C.F. Dong, X.G. Li, Electrochim. Acta 55 (2010) 5990.
[4] W.W. Chen, W. Gao, Electrochim. Acta 55 (2010) 6865.
[5] H.Y. Yang et al., Electrochimica Acta 63 (2012) 131.
[6] A.P. Abbott, G. Capper, K. Mckenzie, K. Ryder, J. Electroanal. Chem., 2007, 599, 288-294.

Electropolymerized Molecularly Imprinted Electrodes for Amylase Sensing

I. M. Miranda*, L. Sousa, C. M. Pereira, F. Silva
Departamento de Química
Faculdade de Ciências da Universidade do Porto
Rua do Campo Alegre 687
4169-007 Porto, Portugal
**ines.miranda@fc.up.pt*

Abstract:

The measurement of protein concentration in aqueous samples is a fundamental assay in biochemistry research. Different proteins, namely enzymes, are involved in countless biological processes and be able to notice alteration on its concentration can be of great interest in diverse areas which goes from Medicine to Environment.

Amylase is known since XIX century, when it was identified in saliva as the initial responsible for starch digestion. Nowadays the mechanism that allows de hydrolysis of big carbohydrates and starch into small molecules like maltose, dextrins and other small monosaccharides is well know and studies about amylase are more focused on applications and consequences of it quantity deregulation in biological systems. (1)

The aim of this work is to build a simple and efficient electrochemical sensor based on a carbon screen printed electrode, molecularly imprinted by electropolymerization (MIPs). Similar systems were already described in literature (2,3).

Molecularly Imprinted Electrodes (MIE) can be used for the indirect quantification of amylase using and electrochemical probe. $[Fe(CN)_6]^{3-}$/ $[Fe(CN)_6]^{4-}$ was chosen as electrochemical active probe and cavities formed by MIP process provides a pathway to its diffusion to electrode surface (4).

Electrochemical impedance spectroscopy (EIS) measurements are performed and the charge transfer resistance of $[Fe(CN)_6]^{3-}$ reduction can be related with Amylase concentration. The effect of experimental parameters and the analytical parameters will be presented and discussed.

Acknowledgments:

Inês Miranda is grateful to FCT for financial support under PhD schoolarship SFRH/BD/75026/2010.

References:

1. S. Schumacher, C. Kirschbaum, T. Fydrich, A. Strohle, *Psychoneuroendocrinology,* 38 (2013) 729—743
2. S. Viswanathan, C. Rani, S. Ribeiro, C. Delerue-Matos, *Biosensors and Bioelectronics*, 33 (2012) 179-183
3. D. C. Apodaca, R. B. Pernites, R. Ponnapati, F. R. del Mundo, R. C. Advincula, *Macromolecules*, 44 (2011) 6669-6682
4. X. Kan, Z. Xing, A. Zhu, Z. Zhao, G. Xu, C. Li, H. Zhou, *Sensors and Actuators B: Chemical*, 168 (2012) 395-401

Development and mathematical analysis of operator splitting techniques applied to multi-scale models of Li-ion batteries

Zénó Farkas[1], István Farago[1], A. Kriston[2]
[1]Eötvös Loránd University, Department of Applied Analysis, Pázmány P. s 1/B, Budapest 1117, Hungary
[2]Institute for Energy and Transport, Joint Research Centre, European Commission,
1755 ZG Petten, The Netherlands
akos.kriston@ec.europa.eu

Li-ion batteries (LIB) are a key enabling technology to store sufficient electricity, in the form of chemical energy, for future electric vehicles (EV) with a desirable driving range. Despite the current rising popularity of EVs, the technology needs to be further improved. Translation of molecular-scale insights into improved products and processes requires on understanding of LIB behavior across a range of length and time scales. Therefore new mathematical modelling approaches are needed to explain how molecular level diffusion, heat transfer and migration processes can influence macroscopic level phenomena such as current, potential and concentration distribution. To successfully describe, design, and control complex electrochemical systems rigorous mathematical analysis of the numerical tools is required.

The mathematical description of LIB is based on a system of time-dependent parabolic partial differential equations (PDE) with a nonlinear source term. The most widely used simulation method is the macrohomogeneous model, because it can predict the macroscopic behavior of LIB. Since it is difficult to solve the coupled PDE on one time and on one length scale, multi-scale models have been developed. In this work, operator splitting techniques [1, 2] have been applied successfully to simulate charge-discharge characteristics of LIB at multiple time and length scales. The operator splitting method is suitable for solving time-dependent complex physical problems, where the operators in the equations describe different sub-processes. During the operator splitting, these sub-processes are separated into different equations so that the original problem can be approached by solving each equation generated by the sub-operators individually. These simplified (decoupled) equations are less complex and easier and faster to solve, however inherit numerical errors due to decoupling. Selection of an stable and accurate scheme can significantly reduce numerical errors. Therefore the operator split LIB numerical model is analyzed in terms of stability, accuracy and processor cost. The qualitative and quantitative errors of schemes are analyzed while applying different kinetic approaches. It is shown that the developed method is suitable for describing fast processes, making real-time monitoring and controlling of LIB possible.

1. Ákos Kriston, György Inzelt, , István Faragó, Tamás Szabó, Simulation of the transient behavior of fuel cells by using operator splitting techniques for real-time applications. Computers & Chemical Engineering, 2010. 34: p. 339-348.
2. István Faragó, Tamás Szabó, Ákos Kriston, An IMEX scheme for reaction-diffusion equations: application for a PEM fuel cell model. Central European Journal of Mathematics, 2013. 11: p. 746-759.

Functional porous materials for redox flow batteries

Mateusz Donten,[1,2,3] Ivan Vakulko,[1] Carole Lainé,[3] Cana Khalouche,[3]
Ievgen Mazurenko,[1] Alain Walcarius,[1] Michel Perdicakis,[1] Andreea Pasc,[2] Mathieu Etienne[1]

[1]LCPME UMR 7564 CNRS – Université de Lorraine
405, rue de Vandoeuvre, Nancy, France
[2]SRSCM UMR 7565, CNRS – Université de Lorraine
BP 70239 Bd des Aiguillettes, Vandoeuvre-les-Nancy, France
[3]Amer-Sil, 61 rue d'Olm, L-8281 Kehlen, Luxembourg
mathieu.etienne@univ-lorraine.fr

The demand for renewable energy, e.g. electricity produced from sun or wind for instance, is actually increasing significantly with the goal to become less dependent from fossil reserves or nuclear sources of energy. The major drawback of renewable energies is their discontinuous production, varying dramatically with time, which makes estimation of production unlikely; moreover, the periods of production does not necessarily fit the periods of consumption [1].

Therefore, the development of renewable energy must be associated to the development of suitable battery technologies displaying low cost, long life-cycle and low maintenance [1,2]. Redox-flow batteries (RFB) are promising devices to exhibit such features. RFB have the characteristic to dissociate the reservoirs for storage of anolyte and catholyte from the electrochemical cell [3–6]

Main components of the battery are the electrolyte, the electrodes and eventually the ion-permeable membrane. Different redox species can be involved in RFB. All-vanadium batteries, the most-successful commercial approach to date, involve only vanadium species in both catholyte and anolyte. It allows minimizing the risk of irreversible mixing of electrolyte in case of defects/cracks or undesired permeability in the membrane separator. Two redox couples are involved in all-vanadium batteries, respectively V^{2+}/V^{3+} and VO^{2+}/VO_2^+ [6].

We will present in this communication our present investigations on the functionalization of porous materials for redox flow batteries, including the modification of membranes and carbon electrodes. These materials have been characterized individually at different scale and implemented in a laboratory prototype of redox flow battery in order to correlate the properties of the materials with their efficiency for energy storage.

[1] Z. Yang, J. Zhang, M.C.W. Kintner-Meyer, X. Lu, D. Choi, J.P. Lemmon, et al., Electrochemical energy storage for green grid., Chem. Rev. 111 (2011) 3577–613.
[2] B. Dunn, H. Kamath, J.-M. Tarascon, Electrical energy storage for the grid: a battery of choices., Science. 334 (2011) 928–35.
[3] M.R. Palacín, Recent advances in rechargeable battery materials: a chemist's perspective., Chem. Soc. Rev. 38 (2009) 2565–2575.
[4] C. Ponce de León, A. Frías-Ferrer, J. González-García, D.A. Szánto, F.C. Walsh, Redox flow cells for energy conversion, J. Power Sources. 160 (2006) 716–732.
[5] P. Leung, X. Li, C. Ponce de León, L. Berlouis, C.T.J. Low, F.C. Walsh, Progress in redox flow batteries, remaining challenges and their applications in energy storage, RSC Adv. 2 (2012) 10125.
[6] M. Skyllas-Kazacos, M.H. Chakrabarti, S.A. Hajimolana, F.S. Mjalli, M. Saleem, Progress in Flow Battery Research and Development, J. Electrochem. Soc. 158 (2011) R55.

Getting graphene from graphite deposited by commercial technique Rocio Pyrolitic

Arturo Nascir Pérez Martínez[1], Erwin Said Guillen López [1], Enrique Cañeda Guzmán[2], Enrique Barrera Calva[3a], Carlos David Hernández Pérez[3a], Maria Luisa Lozano Camargo[1,3b*]

[1]División de Ingeniería Ambiental, Tecnologíco de Estudios Superiores del Oriente del Estado de México. Paraje San Isidro/Av. de las Torres, s/n-Barrio de Tecamacalco, La Paz, Estado de México. Código Postal 56400. México. E-mail: malulozano@gmail.com
[2]Área Académica de Ciencias Básicas, Instituto Tecnológico de Iztapalapa II, Calle Valle de México No 47 Colonia Miravalle de Iztapalapa México, Distrito Federal C.P. 096996, Tels: 2682 03250 y 00455 3929 7303. fmenrique1@gmail.com
[3]Universidad Autónoma Metropolitana-Iztapalapa, área de Ingeniería en Recursos Energéticos[a], Área de Electroquímica[b]. San Rafael Atlixco 186, Col. Vicentina, AP 55-534. México, D.F. C.P. 09340. Tel: +52(55) 58 04 46 71 Ext (19), Fax +52(55) 58 04 46 66.* ebc@xanum.uam.mx

ABSTRAC

We are so accustomed to pencils and seem so simple objects that you might think are time with us. However, none of the ancient civilizations came to know them. For Humanity graphite, which is mine pencils, is almost a newcomer: it was in the sixteenth century when the English found a first deposit of pure graphite, then thought it was lead. In fact even today is called lead, lead in English, mine pencils. Quickly the usefulness of the new material was found to write and its popularity spread worldwide; was given the name of graphite from the Greek word meaning to write. It was not until the late eighteenth century, when the Swedish chemist Carl Scheele, best known for his discovery of oxygen, found that it was actually graphite carbon [1,2]. Later it was found that graphite was formed by several layers of carbon atoms and each layer is what is called graphene; although the link and the chemical structure is known in the early 1930s and the electronic band structure in 1949, obtaining graphene was complicated because it had to separate the layers and the thickness of each is very small, that of an atom carbon; It is also very light, less than 8 grams of graphene sufficient to cover the surface of a football field in 1990, physicists at the University of Aachen in Germany got so thin graphene films that you could see through them; ten years later the thickness had been reduced to a few dozen in 2004 Andrei Geim and Konstantin Novoselov and his team from the University of Manchester "manufactured" graphene, thanks to which the two Russian-born scientists received the Nobel Prize in Physics in 2010 [3,4,5].

This paper presents the first results of the study of obtaining graphene is presented from graphite pencil, and sprinkled pyrolytic deposition, in order to employ a method of obtaining graphene economical and easy to apply.
A new methodology was raised as to obtain this product is established as one of the materials with older applications in the future by the great features that presents, studies for the possible acquisition of Graphene, were corroborated by spectrometric methods as X-ray diffraction, infrared spectroscopy, TEM, and profilometry. The resulting coating of the pyrolytic spray application, it was subjected to various tests to ensure that the desired product is obtained in this case Graphene.

REFERENCES

1) A. K. Geim K. S. Novoselov, the rise of graphene. Nat. Mater.2007, 6, 183-191.
2) P. Avouris Z. H. Chen, V Perebeinos. Carbon-based electronics Nat. Nanotechnol. 2007, 2, 605-615.
3) S. Iijima. Helical microtubules of graphitic carbon Nature. 1991. 354. 56-58
4) S. Stankovich. D. A. Dikin. R. D. Piner. K. A. Kohlhaas. A. Kleinhammes. Y. Jia. Y. Wu. S.
5) T. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon 2007. 45. 1558-1565
6) C.D. Dimitrakopoulos, D.J. Mascaro, *IBM J. Res. & Dev.* **45**, 11 (2001).

Activated carbon obtained by bambu species of African oldhamii by physical activation for be used in air filters

Arturo Nascir Pérez Martínez[1], Erwin Said Guillen López [1], Enrique Cañeda Guzmán[2], Enrique Barrera Calva[3a], Maria Luisa Lozano Camargo[1,3b*]

[1]*División de Ingeniería Ambiental, Tecnologíco de Estudios Superiores del Oriente del Estado de México. Paraje San Isidro/Av. de las Torres, s/n-Barrio de Tecamacalco, La Paz, Estado de México. Código Postal 56400. México. E-mail: malulozano@gmail.com*
[2]*Área Académica de Ciencias Básicas, Instituto Tecnológico de Iztapalapa II, Calle Valle de México No 47 Colonia Miravalle de Iztapalapa México, Distrito Federal C.P. 096996, Tels: 2682 03250 y 00455 3929 7303. fmenrique1@gmail.com*
[3]*Universidad Autónoma Metropolitana-Iztapalapa, área de Ingeniería en Recursos Energéticos[a], Área de Electroquímica[b*]. San Rafael Atlixco 186, Col. Vicentina, AP 55-534. México, D.F. C.P. 09340. Tel: +52(55) 58 04 46 71 Ext (19), Fax +52(55) 58 04 46 66. ebc@xanum.uam.mx*

ABSTRAC

In recent years, there has been a great development of environmental policies, which today require less waste generation from industrial production and greater control over the waste generated. Because of this, there has been a strong impetus to the development of technologies to prevent waste production and the search for environmentally friendly products that generate less waste and less dangerous. Today it is widely implemented the use of activated carbon in various fields of industry [1,2]. Activated carbon is a product that has a similar lattice crystal structure of graphite, it´s extremely porous and may develop surface area of about 1,500 square meters per gram of carbon. The choice of precursor is primarily a function of its availability, price and purity, but the manufacturing process and the possible application of the final product should be considered. Bambu has a 90.03% moisture at 63% char is volatile matter which 35% is coal and the rest is ash. When you start using carbonized bambu carbonization 93% activated carbon and 7% volatile matter in coal washing and sieving 80% yield is obtained due to the loss of these stages is obtained [4,5].

In this paper the results of the synthesis of activated carbon-based Bambu oldhamii African species occurs, this being a material having an excellent alternative in the production of activated carbon at a low cost and environmentally. A characterization of coal obtained under optimum conditions using NMX Standards [3] and physical activation method was performed. Optimal conditions for activation by physical activation activated carbon are T = 550: 98 ° C and t = 122: 76 min resulting in a surface area of 798.4625mg / g, being this an acceptable area in the quality required by the market. Furthermore spectroscopically compared the particle size and morphology by XRD, SEM, these being similar to that of commercial carbon DARCO brand Atlas Chemical Industries Inc. Grade G-60.

REFERENCES

1) Mishra S.B, Langwenya S.P. Study on surface morphology and physicochemical properties of raw and activated South African coal and coal fly ash. En: Physics and Chemistry of the earth. Elsevier. Vol. 35. pp. 811- 814. 2010.
2) Especificaciones de calidad y reactivación del carbón activado, Biblioteca digital Unison, Cap. II. 2006
3) NMX-F-296-SCFI-2011. Industria azucarera y alcoholera determinación del número de yodo en muestras de carbones activados empleados en la refinación de azúcar.
4) M. y Panyathanmaporn, R.-A. (2008). Production of activated carbon from coconut shell: Optimization using response surface methodology. Bioresource Technology 99 (11), 4887-4895.
5) Optimización de la producción de carbón activado a partir de Bambú Bravo-División de Estudios de Posgrado e Investigación - Instituto Tecnológico de Orizaba, Oriente. 9 #852. Col. E. Zapata. C.P. 94320, Orizaba, Ver. México, Vol. 9, No. 3 (2010) 359-366.

Electrocatalysis at the Nanoscale – Oxygen Evolution Reaction (OER) at Single Submicrometric Ni(OH)$_2$ Particles

Jan Clausmeyer, Justus Masa, Wolfgang Schuhmann
Analytische Chemie – Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum,
Universitätsstrasse 150, D-44780 Bochum, Germany
jan.clausmeyer@rub.de

Analysis of single micro- or nanometric objects such as catalytically active nanoparticles or living cells reveals information not accessible to classical techniques for the study of their statistical ensembles. Carbon nanoelectrodes are a versatile platform for multiple sensor designs to perform non-ensemble measurements.[1,2]

The identification of efficient catalysts for the oxygen evolution reaction (OER) remains a key challenge for energy conversion by (photo)electrochemical water splitting. We demonstrate the use of carbon nanoelectrodes for the study of the electrocatalytic properties of single Ni(OH)$_2$ particles, a well-known catalyst for the OER. The nanoelectrodes fabricated from pyrolytic decomposition of butane inside of quartz capillaries are tunable in size from 1 nm to several 100 nm.[3,4]

Ni(OH)$_2$ was electrochemically deposited on the needle-type nanoelectrodes of a few nm in diameter, resulting in single, mostly spherical ß-Ni(OH)$_2$ particles which could be studied individually regarding their activity towards the OER. The particles exhibited high Tafel slopes, in particular at high overpotentials. Yet, high current densities and high turnover numbers of nearly 1000 s^{-1} were found. These observations reflect the high mass transport rates present at submicrometric electrodes which are not accessible by classical hydrodynamic voltammetry.

References

(1) Xiao, X.; Bard, A. J. *J. Am. Chem. Soc.* **2007**, **129**, 9610-9612 .
(2) Chen, S.; Kucernak, A. *J. Phys. Chem. B* **2004,** *108,* 3262-3276.
(3) Actis, P.; Tokar, S.; Clausmeyer, J.; Babakinejad, B.; Mikhaleva, S.; Cornut, R.; Takahashi, Y.; López Córdoba, A.; Novak, P.; Shevchuck, A. I.; Dougan, J. A.; Kazarian, S. G.; Gorelkin, P. V.; Erofeev, A. S.; Yaminsky, I. V.; Unwin, P. R.; Schuhmann, W.; Klenerman, D.; Rusakov, D. A.; Sviderskaya, E. V.; Korchev, Y. E. *ACS Nano*. **2014,** *8*, 875–884.
(4) Clausmeyer, J.; Actis, P.; López Córdoba, A.; Korchev, Y. E.; Schuhmann, W. *Electrochem. Commun.* **2014**, *40*, 28–30.

Multi-scale Approach in Studying the Influence of Annealing Conditions on Conductivity of TiO_2 Nanotubes

M. Santamaria[1], G. Conigliaro[1], F. Di Franco[1], R. Macaluso[2], M. Mosca[2], S. Miraghaei[3], F. Di Quarto[1]

[1] *Electrochemical Materials Science Laboratory, DICAM University of Palermo, Viale delle Scienze,*
90128 Palermo, Italy
monica.santamaria@unipa.it
[2] *Thin Films Laboratory, DEIM University of Palermo, Viale delle Scienze, 90128 Palermo, Italy*
[3]*Department of Mechanical Engineering, Urmia University of Technology, 17165 Urmia, Iran*

Titanium oxide nanotubes (NTs) have attracted much attention during last decade due to their special characteristics such as one-dimensional highly ordered geometry with large surface area and good chemical and optical stability. Titanium dioxide is an environmentally benign photocatalyst with low cost but suffers from dissatisfactory quantum efficiency. Among various routes to produce titanium oxide nanostructures, a simple approach is anodizing metallic titanium in fluoride containing electrolytes [1-2]. Anodizing in fluorides containing bath can be carried out under self-organizing conditions and can be adjusted to lead to highly ordered arrays of closely packed vertically aligned tubes. The tubes after formation are amorphous, but by suitable heat treatment they can be converted to an anatase or rutile crystalline polymorph [1]. For many applications crystallization to anatase turned out to be highly beneficial, as optical and electrical properties of TiO_2 can strongly be modified by heat treatments [3-5]. This happens because titanium oxide is reported to be very sensitive to self-doping during high temperature as a consequence of formation of defects (i.e. Ti^{3+}/O^{2-} vacancy formation). According to previous finding based on global conductivity measurements supported by X-ray diffraction analysis, heat treatment influences the crystallinity of the NTs, the thickness and crystalline structure of the barrier TiO_2 layer beneath the tubular array and therefore the electrical behaviour of NTs [3-5].

In this work we want to study the effect of annealing conditions (temperature, time and atmosphere) on the electrical properties of anodic TiO_2 NTs grown to 45 V in ethylene glycol with addition of 0.25 wt% NH_4F and 0.75 wt% deionized water. Morphology of the NTs was studied by Scanning Electron Microscopy, while their structure was studied by X-ray diffraction. Ex situ solid state electrical conductivity measurements were carried out in order to estimate at the macroscale the resistance of TiO_2 NTs arrays annealed in different conditions. Electrochemical Impedance Spectra (EIS) and Differential Capacitance (DC) curves were also recorded in 0.1 M Na_2SO_4 aqueous solution in order to model the electrical behavior of the metal/electrodes/solution interface at the nanoscale and to identify the contribute of barrier layer and of the tubes in determining the overall resistance.

Photoelectrochemical measurements were also performed to estimate the band gap of the TiO_2 NTs and to get information on the transport properties of the photo-generated carriers.

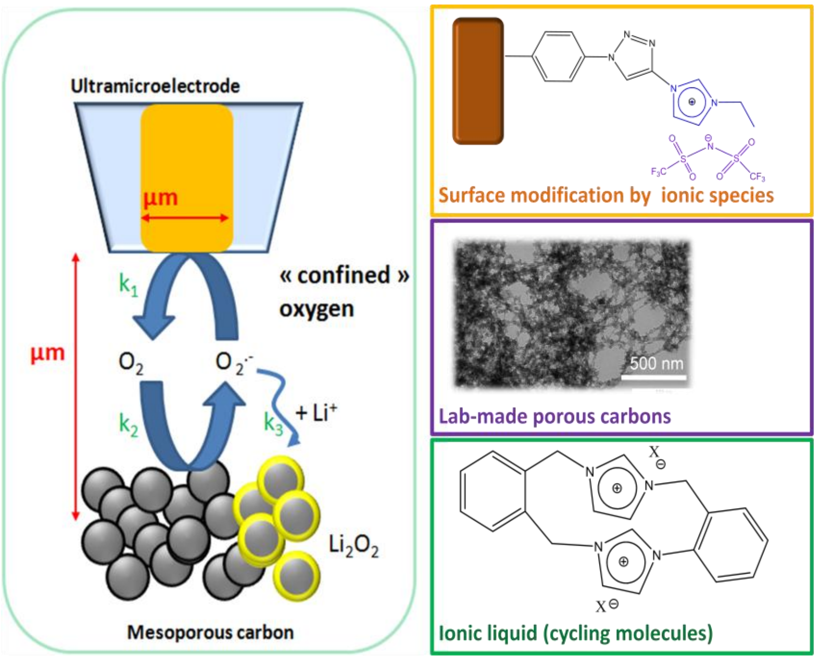
1 - K. Lee, A. Mazare, P. Schmuki, Chemical Reviews, 114 (2014), 9385-9454.
2 - X. Zhou, N.T. Nquyen, S. Özkan, P. Schmuki, Electrochemistry Communications, 46 (2014), 157-162.
3 - S.P. Albu, H. Tsuchiya, S. Fujimoto, P. Schmuki, TiO_2 Nanotubes, Eur. J. Inorg. Chem. 27 (2010), 4351-4356
4 - A. Tighineanu, T. Ruff, S. Albu, R. Hahn, P. Schmuki, Chemical Physics Letters, 494 (2010), 260-263
5 - A. Tighineanu, S.P. Albu, P. Schmuki, Phys. Status Solidi RRL, 8 (2014), 158-162.

How to understand oxygen reduction at porous electrodes in the aprotic lithium-air battery: rotating ring disk investigation or scanning electrochemical microscopy?

Walaa Nasseraldine,[1,2] Ibrahim Bou Malham,[2] Ziad Herro,[2] André Vioux,[1] Ahmad Mehdi,[1] Nicolas Brun,[1] Stefan A. Freunberger,[3] Olivier Fontaine[1]
1. Institut Charles Gerhardt - UMR CNRS 5253, Montpellier, France
2. Laboratoire de Physique Appliquée (LPA), Faculté des sciences II, Université Libanaise, B.P 90656 Fanar Liban.
3. Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

olivier.fontaine@univ-montp2.fr

The lithium-air battery attracts outstanding interest among energy storage devices due to potentially significantly higher energy storage than current batteries. However many challenges remain to make it practical reality.[1] The main reaction during discharge is the famous oxygen reduction reaction. Oxygen is first reduced to superoxide that reacts with lithium ions from the electrolyte to form lithium peroxide (Li_2O_2). This is similar to the formation of hydrogen peroxide in aqueous media but with the difference that Li_2O_2 is a solid that is deposited on electrode surface. A lot of challenges are associated with the understanding of its formation and its reactivity that depends greatly on the chemical environment;[2] particularly (i) solvent, (ii) electrode porosity, (iii) electrode material and its surface.



Oxygen as inner sphere reactant has been studied extensively in aqueous media on flat glassy carbon, gold or platinum. To better grasp its reactivity in porous electrodes in nonaqueous Li^+ electrolytes it needs to be investigated in the porous electrode. In this work we study O_2 reduction in new types of porous electrode materials with surface modifications and electrolytes including ionic liquids containing a range of Li^+ concentrations. Particularly we will compare the insights that rotating ring disc and scanning electrochemical microscopy can provide about the processes occurring in these complex processes.

1. Y. Chen, S. A. Freunberger, Z. Peng, O. Fontaine and P. G. Bruce, *Nat Chem*, 2013, **5**, 489-494.
2. C. Li, O. Fontaine, S. A. Freunberger, L. Johnson, S. Grugeon, S. p. Laruelle, P. G. Bruce and M. Armand, *The Journal of Physical Chemistry C, 2014,* **118**, 3393-3401.

Cyclic Voltammetric Investigation of Electrosynthesized Pyrano[2,3-*d*]Pyrimidinones

Akbar Islamnezhad, Maryam Valizadeh, Hassan Kefayati
Department of Chemistry, Faculty of Science, Islamic Azad University, Rasht Branch, Iran
E-mail: aislamnezhad@iaurasht.ac.ir

Pyrano-pyrimidinones have diverse biological properties such as antitumor, antibacterial, antihypertensive, hepatoprotective, cardiotonic, vasodilator, bronchiodilators and antiallergic activities and some of them exhibit antimalarial, antifungal, analgesics and herbicidal properties [1-5]. In previous work [6], we report the green electrosynthesis of 7-amino-6-cyano-5-aryl-5*H*-pyrano[2,3-*d*]pyrimidine-(1*H*,3*H*)-2,4-diones. To the best of our knowledge, there are no report on cyclic voltammetric investigation of 7-amino-6-cyano-5-aryl-5*H*-pyrano[2,3-*d*]pyrimidine-(1*H*,3*H*)-2,4-diones. Therefore, in this research, we wish to report, for the first time, the cyclic voltammetric evaluation of some of these compounds.

Barbituric acid, aldehyde and malononitrile in ethanolic medium at undivided cell in the presence of potassium bromide as an electrolyte, electro catalytically transformed to the substituted pyrano[2,3-*d*]pyrimidinones with 65-85% yields. The completeness of electrolysis was monitored by cyclic voltammetry (CV) using the µAutolab FRA2 Potentiostat-Galvanostat. A three-electrode system was used with a platinum rod as working electrode, a GC electrode as the counter electrode and an Ag/AgCl as the reference electrode. The structure of products was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. In this electrosynthesis, the first step is electrochemical that follows by chemical reaction. Therefore the proposed mechanism is EC. The cyclic voltammetric investigation of some products showed that these compounds were electroactive in appropriate potentials at the Pt rod-working electrode.

Keywords: *Pyrano[2,3-d]pyrimidinones; Electrosynthesis; Cyclic voltammetry; Electrochemical behaviour*

References:

[1] E.M. Griva, S. Lee, C.W. Siyal, D.S. Duch, C.A. Nichol, J. Med. Chem. 23 (1980) 327.
[2] G.L. Anderson, J.L. Shim, A.D. Broom, J. Org. Chem. 41 (1976) 1095.
[3] M.M. Ghorab, A.A.Y. Hassan, Phosphorus, Sulfur, Silicon Related Elem. 141 (1998) 251.
[4] D. Heber, C. Heers, U. Ravens, Pharmazie, 48 (1993) 537.
[5] J. Davoll, J. Clarke, E.F. Eislager, J. Med. Chem. 15 (1972) 837.
[6] H. Kefayati, M. Valizadeh, A. Islamnezhad, Anal. Bioanal. Electrochem. 6 (2014) 80.

The Studies of the Redox Behaviour of the Hydroquinone/Quinone Couple on Biologically Treated Polyaniline

Elena Binkauskiene, Albinas Lugauskas, Vitalija Jasulaitiene, Virginijus Bukauskas

State Research Institute, Center for Physical Sciences and Technology,
Gostauto Str. 9, LT-01108 Vilnius, Lithuania
elenbink@ktl.mii.lt, lugauskas@chi.lt, vitalijaj@chi.lt, virgis@pfi.lt

Whereas some biochemical compounds in nature have the hydroquinone or quinone section in their structures and many of the by-products of microbial metabolism, including oxalic acid are damaging, the studies of the redox behaviour of the hydroquinone/quinone couple are extremely important [1]. The aim of the presented study was to elucidate the effect of the growth and metabolism of mycobiota on the redox behaviour of the hydroquinone/quinone couple on the biomodified polyaniline surface.

Polyaniline films were synthesized by potentiodynamic polymerization on a nickel electrode in an aqueous oxalic acid solution. The mycobiota of different functional morphology from our culture collection were used during this study.

The results obtained suggest that, the hydroquinone/quinone redox response of the biologically treated electrode depends on the mycobiota species in the biolayer. The electrochemical analysis of the biomodified polymers was completed by X-ray photoelectron spectroscopy, scanning electron and atomic force microscopy. A conspicuous difference in the oxidation levels and oxalate impurities at the polymer surface treated by fungi was confirmed, a higher level of oxalic acid accumulation showed a suppression effect towards hydroquinone electrooxidation [2].

References:
[1] A.M. Polcaro, M. Mascia, S. Palmas, A. Vacca, in Electrochemistry for the environment (Eds: C. Comninellis, G. Chen), Springer, New York Dordrecht Heidelberg London, 2010, pp. 205-227.
[2] E. Binkauskiene, A. Lugauskas, A. Bukauskas, The mycological effect on morphological, electrochemical and redox properties of the polyaniline surface. Surf. Interf. Anal. 45 (2013) 1792.

Voltammetric Rizatriptan Nanobiosensor

Akbar Islamnezhad, Nasibeh kouchaknezhad

Department of Chemistry, Faculty of Science, Islamic Azad University, Rasht Branch, Iran
E-mail: aislamnezhad@iaurasht.ac.ir

Rizatriptan benzoate (RB) belongs to a group of medicines known as serotonin agonists [1]. It is described chemically as: *N*, *N* dimethyl-5-(1*H*-1,2,4-triazol-1-ylmethyl)-1*H*-indole-3-ethanamine mono benzoate. It is used in the treatment of migraines. The literature reveals that various methods for the determination of rizatriptan benzoate are spectrophotometry, gas choromatography, high-performance liquid choromatography, liquid chromatography/tandem mass spectrometry, microemulsion electrokinetic capillary chromatography and reversed-phase liquid chromatographic [2]. The electrochemical biosensors are inexpensive and possess many advantages such as low background current, wide range of potential windows, rapid surface renewal and easy fabrication [3].

In this work, a new nanobiosensor consisting of multiwalled carbon nanotubes (MWCNTs) and bovine serum albumin (BSA) were prepared and utilized for electrode modification. The modified electrode was applied for electrochemical characterization and determination of RB in phosphate buffer solution (PBS, pH = 7) using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Experimental parameters for RB determination, such as scan rate, pH and supporting electrolyte have been optimized. Under the optimum condition, RB could be linearly detected in the concentration range of 1×10^{-2} M to 1×10^{-4} M ($R^2 = 0.9946$). The detection limit was down to around 5×10^{-5} M and maximum current response was obtained at pH=7 phosphate buffer. Since the proposed nanobiosensor exhibits a very good resolution between the DPV peaks of RB, Sumatriptan, Propranolol and Ergotamine, it can be applied for simultaneous detection of RB in the presence of these compounds in pharmaceutical preparations. The results showed that the modified electrode exhibited excellent electrocatalytic activity to RB and showed great promise for simple, sensitive and quantitative detection and screening of RB.

Keywords**:** *Nanobiosensor, Voltammetry, Bovine Serum Albumin, multiwalled carbon nanotubes, Rizatriptan benzoate*

References

[1] B. Mallikarjuna Rao, S. Sangaraju, M. K. Srinivasu, P. Madhavan, M. Lalitha Devi, P. Rajendra Kumar, K.B. Chandrasekhar, Ch. Arpitha, T. Satya Balaji, *J. Pharm. Biomed. Anal.* 41 (2006) 1146–1151.

[2] T. J. Sunder Raj, Ch. Bharathi, M. Saravana Kumar, J. Prabahar, P. N. Kumar, H. Kumar Sharma, K. Parikh, *J. Pharm. Biomed. Anal.* 49 (2009) 156–162.

[3] B. J. Sanghavi, P. Kalambate, S.P. Karna, A. Srivastava, *Talanta*. 120 (2014) 1–9.

Role of surface roughness in the SERS response of Au-nanocavities

M.E.Vela [a], L. A. Guerra [b], M. A. Daza Millone [a], E. Cortes [a], F. Castez [a], B. Auguié [b], R.C.Salvarezza [a] and A. Fainstein [b]
[a] *INIFTA- CONICET Univ. Nac. de La Plata, Suc. 4 C.C. 16, La Plata, Argentina.*
[b] *Centro Atómico Bariloche e Instituto Balseiro, San Carlos de Bariloche, 8400 Río Negro, Argentina*
mevela@inifta.unlp.edu.ar, FAX: 54 221 4254642

Cavity-void metallic arrays constitute excellent substrates for SERS experiments due to the possibility to vary the plasmon-polariton mode energies from the near infrared to the ultraviolet through the tuning of the void height and diameter, and the selection of the appropriate material. In particular the optical properties of Au position it as one of the most studied materials so far with very promising technological applications. Among the different designs of Au substrates, Au sphere-segment void (SSV) arrays have emerged as promising platforms. They can be obtained through electrodeposition using a self-assembled polystyrene spheres template deposited on a cysteamine modified Au-coated glass slide following the procedure developed by Bartlett et al[1]. The deposition rate and time determine the cavity height and in this way the relative contribution of the different plasmon modes. Despite the role of the geometry in the plasmonic behavior some features like nanoscale roughness should be taken into account to interpret the variation in the SERS response among samples prepared in the same way. In this presentation we show results where we have changed the surface roughness either by thermal annealing or electrochemical roughening of Au SSV substrates. We have found a synergic effect in the SERS enhancement involving nanoscale surface roughness and plasmonic modes of the patterned substrates.

[1] P. N. Bartlett, P. R. Birkin and M. A. Ghanem, Chem. Commun.(2000), 1671–1672

Impact of parameters on electrodeposition of nanocrystalline apatite coating on 316L stainless steel

Dinh Thi Mai Thanh[1] , Pham Thi Nam, Nguyen Thi Thom[1], Emmanuelle Kergourlay[2], David Grossin[2], Ghislaine Bertrand[2], Nadine Pebere[2], Sabrina Joly-Marcelin[2], Thai Hoang[1], To Thi Xuan Hang[1], Christophe Drouet[2]
[1]Institute for Tropical Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Street, Cau Giay, Ha noi, Vietnam
[2] CIRIMAT Carnot Institute, UMR CNRS/UPS/INPT 5085, University of Toulouse, ENSIACET, 4 allée Emile Monso, 31030 Toulouse cedex 4, France
Email: thanhvktnd@yahoo.com, dmthanh@itt.vast.vn

316LSS implants are widely used in the field of orthopedic and dental prostheses, due to significant advantages especially in terms of mechanical properties matching those of human bone, as well as their good biocompatibility and corrosion resistance. But in some cases, the 316LSS implants cannot form strong chemical bonds with natural bone and eventually weaken the surrounding bone, causing failure between bone and implant. To overcome this disadvantage, dedicated research was focused on ways to increase the osteo-integration of 316LSS implant materials by coating approaches involving osteoconductive biomaterials such as titanium nitride (TiN) or calcium phosphate ceramics. Among them, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and more generally apatitic systems (such as nanocrystalline biomimetic apatites, noted HAp) are common bioactive materials and have excellent properties such as a high ability to induce bone tissue growth (osteoconduction/induction) and an intrinsic biocompatibility [1,2]. In this work, nanocrystalline apatite (HAp) coatings were prepared on 316L stainless steel (316LSS) substrates by a potentio-dynamic method (potential scanning in the range from 0 to -1.6 V/SCE) in the presence of dissolved $Ca(NO_3)_2$ and $NH_4H_2PO_4$. We report the influence of experimental conditions as temperature, scanning rate, reaction time and pre-treatment of substrate surface on the morphology, structure and composition of the obtained HAp coating. The results show that the purity of the HAp coating was greatly affected by scanning rate and reaction time with rate of 5 mV/s and reaction time of 26.67 min (corresponding 5 cycles) giving better coatings. In addition, the pre-treatment process of substrate surface has completely changed the HAp morphology from coral-like to cylinder shape.

Keywords: 316L Stainless Steel (316LSS); Hydroxyapatite; Nanocrystalline apatite; Coating; electrodeposition, scanning potential.

Reference

[1]. F. Bir, H. Khireddine, A. Touati, D. Sidane, S. Yala, H. Oudadesse. Electrochemical depositions of fluorohydroxyapatite doped by Cu^{2+}, Zn^{2+}, Ag^{+} on stainless steel substrates. Applied Surface Science 2012, 258, 7021- 7030.

[2]. Dinh Thi Mai Thanh, Pham Thi Nam, Nguyen Thu Phuong, Le Xuan Que, Nguyen Van Anh, Thai Hoang, Tran Dai Lam. Controlling the electrodeposition, morphology and structure of hydroxyapatitr coating on 316L stainless steel. Materials Science and Engineering C 2013, 33, 2037 - 2045.

Magneto-electrochemical interactions during phase transitions at nano/micro structured macro-electrodes

D. Fernández, L. Romeral, M.E.G. Lyons
Trinity College Dublin, School of Chemistry & CRANN/AMBER,
College Green, Dublin 2, Ireland
dafernan@tcd.ie

In electrochemical phase transition processes, where solid or gas phases form from an electrolyte, mass-transport and IR drop may become relevant in cases where high throughput is required. This may be the case of many industrial processes such as metal recovery, water purification, fuel cells and so on. Typically, macro-electrodes have been in use for long time with limited efficiency due to precisely mass-transport limitations that lead to low efficiency, due to low space-time yield and low normalized space velocity with an impact on production rates.

New requirements of low-energy consumption yet intensive production factories impose the need to adequate electrodes in order to comply. Good potential alternatives arise from electrode arrays that involve built-in nano/micro structures, provided that there is a mechanism that supports fast replenishment of reagents to and removal of species from the active surface.

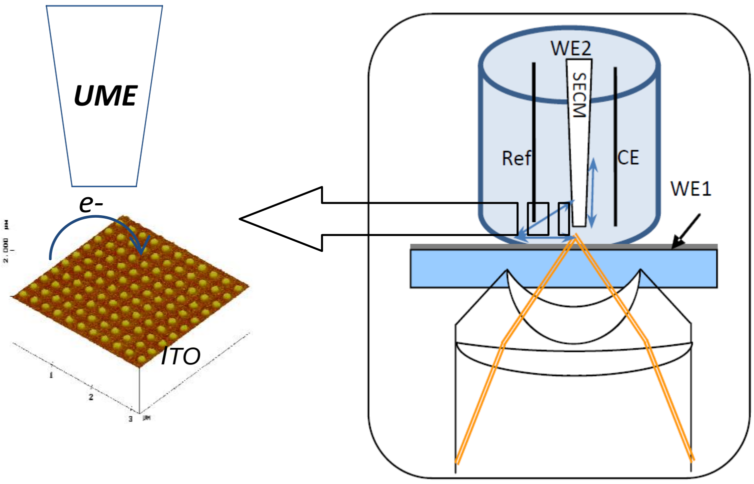
Switching from typical bi-dimensional macro-electrodes to the nano-structured macro-electrodes could provide an alternative for achieving better performances but it is still far from the expected industrial targets. Therefore alternative or complementary techniques to improve efficiency are required.

It is well known that magnetic fields coupled with electric fields enhance mass transport via de Lorentz and other forces. In this work, the applications and properties of nano/micro-structured arrays subject to magnetic field interactions are examined and compared with the traditional bi-dimensional electrodes. Various cell configurations and electrolyte are studied for the deposition of metallic copper from solution, and the production of hydrogen and oxygen gas from water. The results are discussed in terms of recovery yield versus cell efficiency for the estimated active surface areas.

Combining SECM and fluorescence microscopy : a way to investigate electrochemically monitored luminescence on plasmonic electrodes.

Fabien Miomandre[1], Clarisse Tourbillon[1], Jean-Frédéric Audibert[1], Pascal Martin[2], J.C. Lacroix[2]
[1]*PPSM – Ecole Normale Supérieure de Cachan, 61 Avenue du Président Wilson, 94235 CACHAN (France)*
[2]*ITODYS – Université Paris Diderot, 15 rue Jean de Baïf, 75235 PARIS Cedex 13*
mioman@ens-cachan.fr

Fluorescence microscopy and SECM are both techniques that allow measuring luminescence and electrochemical properties at a very local scale. We have shown how fluorescence microscopy especially in Total Internal Reflection (TIRF) configuration can be implemented to follow the electrochemical tuning of luminescence properties of various fluorophores in solution[1-3].



In the case of plasmonic electrodes made of gold nanoarrays we recently observed that both the luminescence and the reflectivity can be electrochemically monitored in the same experiment and in various directions depending on the charge of the electroactive species [4]. In that case the microscope coverslip coated with the gold nanoarrays is used as the working electrode (WE1) whose potential is used to monitor the luminescence. Combining with SECM with TIRF microscopy (see scheme above) allows using a second working electrode (WE2) able to measure the electrochemical properties directly on the grating zone, at the same time the electrochemical modulation is applied and the luminescence features analyzed. Other configurations in which the SECM tip is used to regenerate the fluorophore can also be envisaged. Preliminary results using this combination of techniques will be shown and discussed.

References :

[1] F. Miomandre, C. Allain, G. Clavier, J.F. Audibert, R.B. Pansu, P. Audebert, F. Hartl, Coupling thin layer electrochemistry with epifluorescence microscopy: An expedient way of investigating electrofluorochromism of organic dyes, Electrochem. Commun., 13 (2011) 574-577.

[2] F. Miomandre, E. Lepicier, S. Munteanu, O. Galangau, J.F. Audibert, R. Meallet-Renault, P. Audebert, R.B. Pansu, Electrochemical Monitoring of the Fluorescence Emission of Tetrazine and Bodipy Dyes Using Total Internal Reflection Fluorescence Microscopy Coupled to Electrochemistry, Acs Appl. Mat. Int., 3 (2011) 690-696.

[3] P. Audebert, F. Miomandre, Electrofluorochromism : from molecular systems to set-up and display, Chemical Science, 4 (2013) 575-584.

[4] C. Tourbillon, F. Miomandre, J.F. Audibert, M. Lepeltier, P. Martin, P. Lacroix, Electrochemical modulation of reflectivity and luminescence on plasmonic gratings investigated by fluorescence microscopy coupled to electrochemistry, Electrochim. Acta (2015) in press.

Improvement of the corrosion resistance of Ni-W coatings on steel using a mixed silane film

M.E.Vela, M.P. Quiroga Argañaraz, G.Benítez, A.Rubert, E.D.Prieto, L.M.Gassa, R.C.Salvarezza and J. M.Ramallo-López
INIFTA- CONICET Univ. Nac. de La Plata, Suc. 4 C.C. 16, La Plata, Argentina.
mevela@inifta.unlp.edu.ar, FAX: 54 221 4254642

Self-assembly constitutes a simple method to modify surfaces that drastically changes properties like wettability and hydrophobicity, corrosion resistance and opens multiple strategies of postfunctionalization. In this presentation we show the surface characterization and the electrochemical behavior of Ni-W nanostructured coatings electrodeposited on carbon steel [1,2] that were post-functionalized with two types of silanes. In the first step a silica-rich layer was formed by the reaction of tetraethoxysilane (TEOS) solution in toluene with the surface oxides of the alloy. After this treatment the sample was immersed in an hexane solution of octadecyltrichlorosilane (OTS). The silanized surface was rinsed exhaustively with hexane. After this procedure the XPS analysis showed that the Ni and W signals almost disappeared and that the Si and C signals are the most significant in the spectra. The silanization procedure increases the contact angle from $\theta = 70°$ for the bare Ni-W sample up to $\theta \approx 110°$. The typical cauliflower topography of the nanostructured Ni-W coating was not altered by the functionalization indicating a conformal coverage of the TEOS and OTS self-assembled layers. The nanomechanical properties of the silanized samples were studied by AFM and a rigid behavior was observed in practically all the surface. In those force curves were the layer could be indented, a thickness of 2-20 nm was obtained which exceeded the expected monolayer value. The electrochemical behavior of the TEOS&OTS Ni-W coatings was studied in phosphate-borate buffer (0.1 M KH_2PO_4 + 0.05 M $Na_2B_4O_7$) pH 8.00 with the addition of 1 M Na_2SO_4, an aggressive ion in neutral and alkaline solution, through cyclic voltammetry, following the temporal evolution of the open circuit potential and registering polarization curves at 2 mV/s. Our results showed that the two-step silanization procedure improves the corrosion resistance of Ni-W coated steel preserving their mechanical properties.

[1] M.P. Quiroga Argañaraz, S.B. Ribotta, M.E. Folquer, L.M. Gassa, G. Benítez, M.E. Vela, R.C. Salvarezza, Electrochim. Acta, 56 (2011) 5898

[2] M.P. Quiroga Argañaraz, S.B. Ribotta, M.E. Folquer, E. Zelaya, C. Llorente, J.M. Ramallo-López, G. Benítez, A. Rubert, L.M. Gassa, M.E. Vela, R.C. Salvarezza, Electrochim. Acta, 72 (2012) 87

Energy Storage Device Electrodes from Biomass Fibers and Biofilm

M. Deraman[1,]*, W.M.H. Husin[1], N.H. Basri[1], B. Yatim[1], N.S.M. Nor[1], E. Taer[2], Awitdrus[2], R. Rarma[2],
M.A.R. Othman[1], R. Omar[1] and M.R.M. Jasni[1]
[1]*School of Applied Physics, Faculty of Science and Technology,*
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
[2]*Department of Physics, University of Riau, 28293 Simpang Baru, Riau, Indonesia*
**madra@ukm.edu.my/mderaman113@gmail.com*

Area of research and development in improving electrode materials performance used in an energy storage system such as electrochemical energy storage systems, for example, electric double layer capacitor (EDLC) is to date on a growing rate because the electrode property is one of the critical factor that influence the overall performance of the device. Highly porous carbon electrodes from biomass precursors [1], which have been widely used as electrode material in such a device system, have been chemically and/or physically modified intensively by many researchers to achieve higher device performance [2,3,4]. In our present paper, we report a modification approach that involves the use of graphene/disordered-carbon directly prepared from starch films by carbonization [5] as an additive in the green monoliths of self-adhesive carbon grains from biomass fibers, where these green monoliths are converted by carbonization and activation into highly porous carbon electrodes for application in the EDLC. The pore characteristic of the electrodes is investigated by a nitrogen adsorption-desorption isotherms method, and electrochemical performance of the EDLC is investigated by electrochemical-impedance-spectroscopy (EIS), galvanostatic-charge-discharge (GCD) and cyclic-voltanmmetry (CV) methods.

[1] R. Farma, M. Deraman, Awitdrus, I. A. Talib, E. Taer, N. H. Basri, J. G. Manjunatha, M. M. Ishak, B. N. Dollah and S. A. Hashmi, Preparation of a highly porous binderless activated carbon electrode from fibers of oil palm empty fruit bunches for application in supercapacitors, Bioresource. Technol., 132 (2013): 254-261.
[2] N. H. Basri, M. Deraman, S. Kanwal, I. A. Talib, J.G. Manjunatha, A.A. Aziz and R. Farma, Supercapacitors using binderless composite monolith electrodes from carbon nanotubes and pre-carbonized biomass residues, Biomass Bioenergy, 59 (2013): 370-379.
[3] B.N.M. Dolah, M. Deraman, M.A.R. Othman, R. Farma, E. Taer, N.H. Basri, I.A. Talib, R. Omar, N.S.M. Nor. A method to produce binderless supercapacitor electrode monoliths from biomass carbon and carbon nanotubes. Materials Research Bulletin, 60 (2014):10-19.
[4] N.S. M. Nor, M. Deraman, R. Omar, Awitdrus, R. Farma, N.H. Basri, B.N. M. Dolah, N.F. Mamat, B. Yatim, M.N.M. Daud, Influence of gamma irradiation exposure on the performance of supercapacitor electrodes made from oil palm empty fruit bunches, Energy, 79 (2015) 183-194.
[5] S.J. Byun, H. Lim, G.Y. Shin, T.H. Han, S.H. Oh, J.H. Ahn, H.C. Choi, T.W. Lee, Graphenes converted from polymers. J. Phys. Chem. Lett., 2(2011), 493-497.

Electrochemical properties of Tin phosphide composite anode for Sodium ion Batteries

Gumjae Park, Sungju Sim, and Sang-Min Lee
Battery Research Center, Korea Electrotechnology Research Institute,
12, bulmosan-ro 10beon-gil, Seongsan-gu, Changwon-si, Gyeongsangnam-do 642-120,
Republic of Korea
gjpark@keri.re.kr

Nowadays, the demand for advanced large scalable energy storage system is rapidly increasing for the efficient use of electrical energy and peak-shift operations. Among energy storage systems, rechargeable lithium ion batteries are most successful energy storage system for portable devices and hybrid electric vehicle. However, lithium ion batteries are not suitable for large scale energy storage system due to low abundance of lithium source causing the growing price. Recently, sodium-ion batteries are considered an attractive energy storage system to alternative of lithium ion batteries in the viewpoint of low cost due to the abundance of Na.[1] However, this limits the range of potential candidates for anode materials because of larger size of Na. It is well known that graphite and silicon are suitable for lithium ion batteries, but are not suitable for sodium ion batteries [2-3]. Therefore, many research groups have been focused on the Na-alloys anode using metallic and intermetallic host such as Sn, Sb, and P.[4-6] Na-alloy anodes exhibit very high capacity, but accompany huge volume expansion of the Na-alloy materials.

Metal phosphides (MP_x, M = Sn, Ni) also have received much attention as anode material for Sodium ion batteries due to high reversible capacity at relatively low potential.[7-9] However, most MP_x suffers from a relatively large irreversible capacity due to the decomposition of Na_xM, Na_xP, and metal during cycling. In order to improve the electrochemical properties, MP/C composite have been suggested and some of them prove to be effective in improving the cycle performance.[7] Kim et. al. reported the electrochemical properties and reaction mechanism of nanoparticle Sn_4P_3/C anode for sodium ion batteries.[8] It showed high reversible capacity and good cycle performance.

Here, we synthesized a Sn_4P_3/C using various carbon sources and Sn_4P_3/MP composite alloy to increase the reversible capacity and enhance the cycle performance. We investigated the differences in physical and electrochemical properties between Sn_4P_3 and their composite anodes, examined using powder X-ray diffraction, SEM, and TEM, and galvanostatic charge-discharge test.

References

1. V. Palomares, P. Serras, I. Villaluenga, K. Hueso, J. Carretero-Gonzalez, T. Rojo, *Energy Environ. Sci.* 5 (2012) 5884.
2. P. Ge and M. Fouletier, *Solid State Ionics*, 28-30 (1988) 1172.
3. S. Hong, Y. Kim, Y. Park, A. Choi, N. Choi, K. Lee *Energy Environ. Sci.* 6 (2013) 2067.
4. H. Zhu; Z. Jia, Y. Chen, N. Weadock, J. Wan, O. Vaaland, X. Han, T. Li, L. Hu, *Nano Lett.* 13 (2013) 3093.
5. L. Xiao, Y. Cao, J. Xiao, W. Wang, L. Kovarik, Z. Nie, J. Liu, *Chem. Commun.* 48 (2012) 3321
6. Y. Kim, Y. Park, A Choi, N. Choi, J. Kim, J. Lee, J. Ryu, S. Oh, K. Lee, *Adv. Mater.* 25 (2013), 3045
7. W. Li, S. Chou, J. Wang, J. Kim, H. Liu, S. Dou, *Adv. Mater.* 26 (2014) 4037.
8. Y. Kim, Y. Kim, A. Choi, S. Woo, D. Mok, N. Choi, Y. Jung, J. Ryu, S. Oh, K. Lee, *Adv. Mater.* 26 (2014) 4139.
9. J. Fullenwarth, A. Darwiche, A. Soares, B. Donnadieu, L. Monconduit, *J. Mater. Chem. A* 2 (2014) 2050.

New morphologies of nanostructures obtained by Zn anodization under flowing conditions

J. García-Antón, R. Sánchez-Tovar, R.M. Fernández-Domene, D.M. García-García, M.T. Montañés
Ingeniería Electroquímica y Corrosión, Instituto de Seguridad Industrial, Radiofísica y Medioambiental,
Departamento de Ingeniería Química y Nuclear, Universitat Politècnica de València,
Camino de Vera s/n, 46022 Valencia, Spain
jgarciaa@iqn.upv.es

Nowadays, the use of nanostructures is gaining increasing interest owing to the unique properties that they can provide. In this way, nanostructures can be tailored to possess a characteristic nanosize, high surface area and porosity. Titanium dioxide (TiO_2) nanostructures have a wide application in the energy and environmental fields [1], that is in dye-sensitized solar cells, hydrogen production and photocatalysis, moreover, TiO_2 nanostructures might be used in other related fields such as biomedicine. Apart from TiO_2, ZnO and ZnS are n-type semiconductors with similar band gap to TiO_2 that could be used as low-cost photocatalyzers for H_2 production or dye photodegradation. Another advantage is that the use of hetero-nanostructures could reduce electron-hole recombination processes [2].

In this work, anodization of Zn in Na_2S and NH_4F electrolytes has been carried out. In this way, hetero-nanostructures of ZnO and ZnS with new morphologies have been formed. The influence of Na_2S concentration, water content and hydrodynamic conditions on the morphology of the nanostructure have been studied in detail.

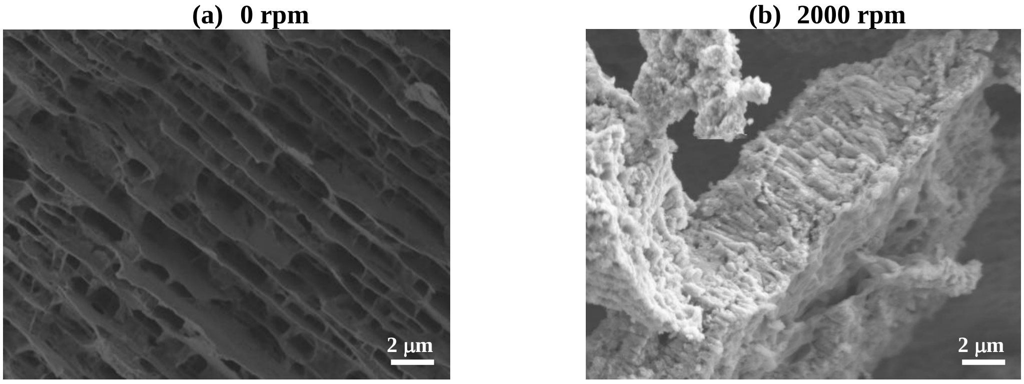


Figure 1. Scanning Electron Microscope images (SEM) of Zn nanostructures anodized in 0.06 M Na_2S and 0.025M NH_4F at 30V during 1h under static (a) and under flowing conditions: 2000 rpm (b).

Figure 1 shows that under static conditions hetero-ZnO and ZnS -nanosheets were obtained; however, under hydrodynamic conditions self-organized nanotubes could be formed. The use of hetero ZnO-ZnS nanotubes increased the transfer of electrons and reduced the hole-electron recombination processes. According to these facts, the efficiency of this type of Zn nanostructures as photocatalyzers is increased.

[1] K. Maeda, K. Domen, Journal of Physical Chemistry Letters 1, 2655-2661, 2010.

[2] Z. Wang, S.-W. Cao, S. C. J. Loo, C. Xue, Crystal Engineering Communications 15, 5688-5693, 2013.

WO_3 photoanodes for hydrogen production

J. García-Antón, R.M. Fernández-Domene, R. Sánchez-Tovar, D.M. García-García, M.J. Muñoz-Portero
Ingeniería Electroquímica y Corrosión, Instituto de Seguridad Industrial, Radiofísica y Medioambiental,
Departamento de Ingeniería Química y Nuclear, Universitat Politècnica de València,
Camino de Vera s/n, 46022 Valencia, Spain
jgarciaa@iqn.upv.es

Tungsten trioxide (WO_3) is an n-type semiconductor with a band gap of 2.6-2.8 eV and an appropriate band position for photoelectrochemical water splitting. For this reason, photoanodes based on WO_3 has attracted great interest as a substitute of TiO_2 photocatalyzers. It is desirable for a photocatalyzer to have a high specific surface area. Therefore, nanotube, nanorod and nanosheet morphologies are desirable for this application.

In this work, anodization of tungsten has been carried out in different electrolytes. That is, 0.2M NH_4NO_3 at 10V and 25ºC during 30 minutes and 1.5M HNO_3 at 20V at 50 ºC during 4 hours. After anodization, samples were annealed at 500 ºC in presence of oxygen for different times. The morphology of the samples was characterized by Scanning Electron Microscopy (SEM), and their crystalline structure by means of Raman Confocal Spectroscopy. Additionally, photoelectrochemical water splitting tests in 0.1M Na_2SO_4 solutions were performed.

According to the results, WO_3 nanostructures are suitable to be used as substitutes of TiO_2 photoanodes for hydrogen production. However, in order to use the nanostructures as photocatalyzers for hydrogen production, samples must have a crystalline structure. Raman spectra reveals that WO_3 nanostructures obtained in nitric acid solutions possess a crystalline structure before annealing that could be improved after heating at 500ºC. On the other hand, Figure 1 shows that nanostructures obtained in ammonium nitrate solutions needs to be annealed at 500ºC for at least 3 hours in order to obtained crystalline WO_3 structures.

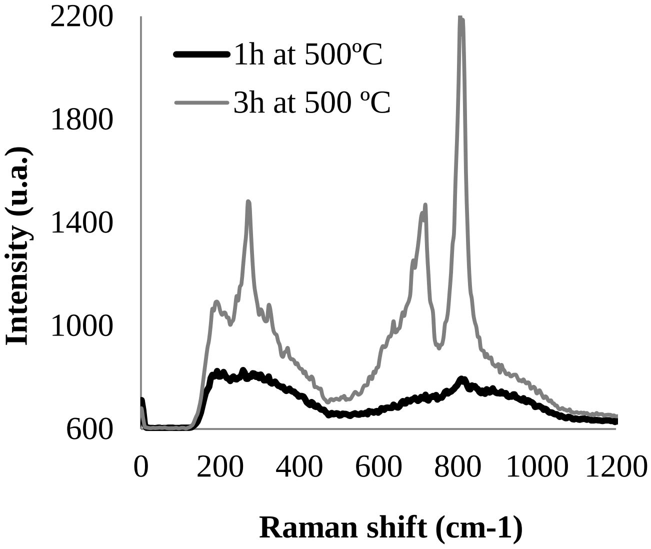


Figure 1. Raman spectra of the WO_3 nanostructures obtained in 0.2M NH_4NO_3 at 10V after annealing at 500ºC for 1 and 3 hours.

Influence of Co Content on Structure and Electrochemical Performance of $Li_{7/6}Mn_{1/2-x}Ni_{1/6}Co_{1/6+x}O_2$(x=0, 1/12, 1/6) as Cathode Materials

Yufang Chen*, Kai Xie, Chunman Zheng, Yujie Li,Yi Pan
College of aerospace science and engineering, National university of defense technology.
Changsha, Hunan, China
E-mail:chenyufang313@126.com

Li- and Mn-rich cathode materials win huge attentions due to their extremely high capacity and unique solid solution composite structure. As a composition contains two or more phase, the compatibility of these phases would be critical points to promise high capacity output. We chose both layered structures which have similar oxygen ion arrangement as framework and distinct cations distribution,[1] to found the xLi_2MnO_3-$yLiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode materials. From former researches,[2] Co was always used to enhance the order of the layered structure. Thus, the Co content was changed to adjust the compatibility of the two contained phase. All the precursors of three samples were synthetized though co-precipitation route, after drying and mixing with lithium, the powders were sintered at 900 °C for 15h to obtain the final products. The XRD (X-ray diffraction) were used to investigate the order and crystal structure of these cathode materials, indicating that the ordering of the layered structure was improved by Co substituted Mn. The intensity of characteristic peaks for monoclinic phase decreases with increasing Co content while the ratio of $I_{(003)}/I_{(104)}$ increase from 1.6181 through 1.6992 to 1.7524, these results combined with the broaden and split more clearly of (006)/(102) and (108)/(110) doublets indicate the formation of more ordered layered structure as Mn was substituted by Co. Electrochemical performance was evaluated by galvanostatic mode at C/10 with cutoff voltage of 4.8V and 4.6 V. Results show that the more Co in the structure, the lower polarizing voltage can be obtained, otherwise, the much lower first cycle coulombic efficiency accompanied. Rate capability (not shown) can be improved but with much faster capacity fade and voltage decay.

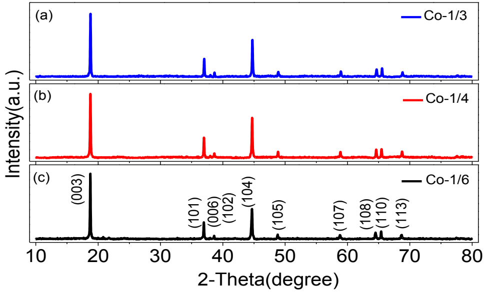


Figure 1XRD pattern of the $Li_{7/6}Mn_{1/2-x}Ni_{1/6}Co_{1/6+x}O_2$(x=0, 1/12, 1/6) (a. total Co-1/3, b. total Co-1/4, and c. total Co-1/6)

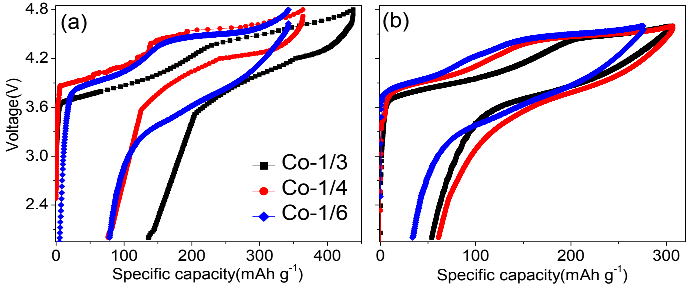


Figure 2 First charge-discharge curves of the $Li_{7/6}Mn_{1/2-x}Ni_{1/6}Co_{1/6+x}O_2$(x=0, 1/12, 1/6, total Co-1/3, Co-1/4, and Co-1/6) at various cutoff voltage (a. 4.8V, b. 4.6V).

Reference

1. Chen, Y.; Chen, Z.; Xie, K., Effect of Annealing on the First Cycle Performance and Reversible Capabilities of Lithium-Rich Layered Oxide Cathodes. *The Journal of Physical Chemistry C* **2014**.

2. Watanabe, S.; Kinoshita, M.; Nakura, K., Capacity fade of LiNi(1−x−y)CoxAlyO2 cathode for lithium-ion batteries during accelerated calendar and cycle life test. I. Comparison analysis between LiNi(1−x−y)CoxAlyO2 and LiCoO2 cathodes in cylindrical lithium-ion cells during long term storage test. *J. Power Sources* **2014,** *247* (0), 412-422.

The Electrochemically Active Complexes Formation in the Ion Discharge from Aqueous Electrolytes

V.S. Kublanovsky, O.L. Bersirova
V.I.Vernadskii Institute of General and Inorganic Chemistry,
32-34 Prospect Palladina, 03680 Kiev-142, Ukraine,
e-mail: kublanovsky@ionc.kar.net

The usual methods for determining the composition of electrochemically active complexes are based on the fact that only one complex in equilibrium with the complex that is dominant in the bulk of the electrolyte is discharge on the electrode. It is evident that the overwhelming majority of electrochemical systems are characterized by quite a number of complex compounds in the bulk of the electrolyte and in the electrode layer. It is also quite logical to think that metal ions are discharged from all or several ionic species that are present in the bulk of the electrolyte or are formed in the cathode layer and on the electrode surface in a particular case, a single species may be such an electroactive species.

We have developed methods for determining electroactive ionic species on the basis of the method developed earlier for determining all concentrations on the electrode surface. New electrochemical functions are proposed: "discharging ion complexity", which relates formation constants to electrode reaction parameters, and "average coordination number of discharging ion", which indicates the composition of discharging complexes.

The study of equilibriums in the bulk electrolyte and in the cathode layer as a function of the ratio of the main solution components, pH and polarizing current density in conjunction with electrochemical parameters makes it possible to establish, by using the proposed theory, the composition of EAC’s that are directly involved in the electrode reaction during the reduction of complexes and hence to control electrochemical processes.

The proposed theory and methods permit one, unlike conventional ones, to investigate electrochemical systems containing no excess ligand (ligands) when several complex metal compounds are present in the electrolyte in comparable amounts and one or several electroactive complexes are directly involved in the electrode process.

Method for determining electrochemically active and electrochemically inactive ions are shown for the discharge of cadmium, zinc, silver and cooper coordination compounds with complexones and halide ions.

Publications are based on the research provided by the grant support of the State Fund For Fundamental Research (project N Φ50/017-2014)

Oxidation of Palladium: Nanoscale Effects in the Deactivation Toward Alcohols Electrooxidation

Lianqin Wang[a,b], Marco Bellini[a], Manuela Bevilacqua[a], Yanxin Chen[a,b], Jonathan Filippi[a], Alesandro Lavacchi[a], Andrea Marchionni[a], Hamish Miller[a], Francesco Vizza[a]
[a]Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), National research Council (CNR)
Via Madonna del Piano 10, 50019, Sesto Fiorentino, Italy
[b]University of Trieste
Via L. Giorgieri 1, 34127 Trieste, Italy
lwang@iccom.cnr.it

Palladium has been explored in recent years for its potential in electrocatalysis. Nanostructured palladium materials have been used in anodes for i) alkaline direct alcohol fuel cells and ii) for the electrochemical reforming of alcohols for the concomitant production of hydrogen and chemicals [1, 2].

The main issue still hampering the full exploitation of nanostructured Pd as catalyst for the electrochemical oxidation of alcohols is its lack of stability. In this investigation we have employed electron microscopy to identify the evolution of the morphology of palladium as a consequence of its oxidation together with X-ray absorption for assessing the evolution of the palladium chemical.

From scanning and transmission electron microscopy we have identified that palladium oxidation may result in significant surface roughening. Meanwhile, PdO is not possible to remove by electrochemical methods. This fact has dramatic implication in the catalytic activity.

X-ray absorption near-edge structure (XANES) (Fig. 1) of the electrode surface has revealed that the exposure at anodic potential lead to the formation of Pd(II) which is not active toward alcohols oxidation. Interestingly the formation of such oxide has been observed in a membrane electrode assembly of alkaline direct ethanol fuel cell after 10 hrs. of work at constant current density of 20 mA/cm^2.

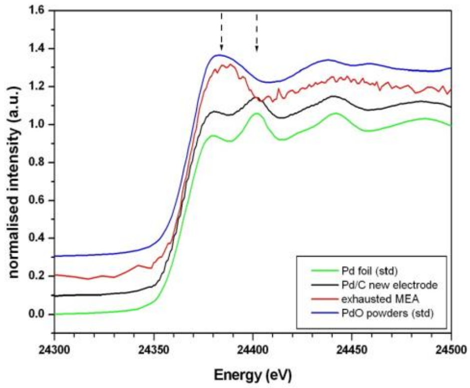


Figure 1 Normalized XANES spectra of standard Pd foil, new Pd/C before DEFC test, exhausted Pd/C after DEFC test and standard PdO powders.

We conclude that palladium oxidation results in the Pd deactivation at the electrode surface. According to our finding, there is the need to design the direct ethanol fuel cells employing palladium operating at anode potentials lower than 0.6 V vs. RHE in order to avoid large anodic stresses of the catalysts.

Acknowledgements

We gratefully acknowledge the European Union for the collaborative project 'DECORE' COOPERATION FP7-NMP-2012-SMALL-6nmp4-sl-2012-309741 and the Ente Cassa di Risparmio di Firenze for the project HYDROLAB.

References

1. V. Bambagioni, C. Bianchini, Y. X. Chen, J. Filippi, P. Fornasiero, M. Innocenti, A. Lavacchi, A. Marchionni, W. Oberhauser and F. Vizza, *Chemsuschem*, 2012, 5, 1266-1273.
2. Y. X. Chen, A. Lavacchi, H. A. Miller, M. Bevilacqua, J. Filippi, M. Innocenti, A. Marchionni, W. Oberhauser, L. Wang and F. Vizza, *Nat Commun*, 2014, 5.

Mathematical modeling and experimental study of current distribution in PEM water electrolyser

Sergey Grigoriev[1], Alexander Kalinnikov[2], Jan Van Der Merwe[3], Dmitri Bessarabov[3]
[1] *National Research University "Moscow Power Engineering Institute",*
Krasnokazarmennaya str., 14, 111250, Moscow, Russia
sergey.grigoriev@outlook.com
[2] *National Research Center "Kurchatov Institute",*
Kurchatov sq., 1, 123182, Moscow, Russia
[3] *DST HySA Infrastructure Centre of Competence, Faculty of Engineering, North-West University,*
Private Bag X6001, Potchefstroom, 2520, South Africa

Hydrogen production by using water electrolysis with proton-exchange membranes (PEM) is widely used in industrial applications [1] and is believed to be promising for renewable energy storage [2]. Durability of PEM water electrolysers must meet long-term operational requirements, especially, if PEM water electrolysers are expected to operate in the MW scale and at a high current density. One of the key parameters responsible for durability and efficiency of a PEM electrolyser is the value and uniformity of electric current in system "electrocatalytic layer – current collector – flow-field plate". Uneven current distribution could create hot spots leading to the failure of a PEM electrolyser [3]. Various characterization and modeling tools are further required to understand characteristics of PEM electrolysers [4,5]. Mathematical model calculations have been used to analyze the current distribution over flow-field plate. Current distribution was calculated as a function of nonuniformity of contact with electrocatalytic layer and electronic conductivity of electrocatalytic layer**.** Theoretical results were compared with the experimental data generated with a sensor plate inserted into the single cell of PEM electrolyser.

Financial support from the Ministry of Education and Science of the Russian Federation (government task No. 2014/123 for performance of the government works in scientific activities) is acknowledged.
Financial support from the DST HySA Infrastructure project KP5 is acknowledged.

References

[1] S.A. Grigoriev, V.I. Porembsky, V.N. Fateev "Pure hydrogen production by PEM electrolysis for hydrogen energy" // International Journal of Hydrogen Energy, 2006, vol. 31, issue 2, pp. 171-175.
[2] F. Barbir "PEM electrolysis for production of hydrogen from renewable energy sources" // Solar Energy 78 (2005) 661-669.
[3] P. Millet, A. Ranjbari, F. de Guglielmo, S.A. Grigoriev, F. Aupretre "Cell failure mechanisms in PEM water electrolyzers" // International Journal of Hydrogen Energy, 2012, Vol. 37, Issue 22, November 2012, pp. 17478-17487.
[4] C.A. Martinson, G. van Schoor, K.R. Uren, D. Bessarabov "Characterisation of a PEM electrolyser using the current interrupt method" // International Journal of Hydrogen Energy, Volume 39, Issue 36, 12 (2014) 20865-20878.
[5] Jan van der Merwe, Kenny Uren, George van Schoor, Dmitri Bessarabov "Characterisation tools development for PEM electrolysers" // International Journal of Hydrogen Energy, Volume 39, Issue 26, 3 (2014) 14212-14221.

Three-dimensional Hierarchical TiO_2 Nanotubes - Carbon Nanofiber Nanostructure as an Anode for High Energy and Power Lithium Ion Batteries

Taeseup Song[1], Hyunjung Park[2], Jihoon Seo[2], Yeon-Gil Jung[3] and Ungyu Paik[2]
[1]Department of Materials Science Engineering, Hanyang University, Seoul 133-791, Korea
[2]Department of Energy Engineering, Hanyang University, Seoul 133-791, Korea
[3]School of Nano and Advanced Materials Engineering, Changwon National University, Changwon 641-773, Korea
e-mail address: upaik@hanyang.ac.kr

The low electrical conductivity of TiO_2 electrodes as well as the high electric resistance between an electrode and a current collector represents a major obstacle to its practical use as an anode for lithium ion batteries. In this study, we report TiO_2 nanotube branched on carbon nanofiber nanostructure, that is capable of providing low electric resistance between the current collector and branched TiO_2 nanotube via carbon nanofiber as well as high TiO_2 nanotubes loading, to achieve both the excellent rate capability and the area energy density. Based on the detailed experimental results and associated theoretical analysis, we demonstrate that the introduction of carbon nanofibers with direct electric contact with current collector enables significant increase in area capacity as well as excellent rate capability. The TiO_2 nanotube branched on carbon nanofiber electrode delivers about 10 times higher area energy density and comparable rate capability compared to those of TiO_2 nanotubes array, directly grown on the current collector.

Photoelectrochemical screening of water splitting catalysts

Daniel Kimmich, Carsten Dosche; Gunther Wittstock
Carl von Ossietzky University, Department of Chemistry, D-26111 Oldenburg
daniel.kimmich@uni.oldenburg.de

Due to the changes in the energy market a sustainable way to produce hydrogen is needed. We search for new catalysts for photoelectrochemical water splitting. Due to the high overpotential, this reaction is often limited by the oxygen evolution reaction (OER). Oxides of 3d transition metals are promising semiconductors for the OER. To date no single material has satisfied simultaneously the different requirements. To find the fittest catalyst from many different elemental compositions, a combination of library preparation and screening has been demonstrated with remarkable success.[1,2] Typical a readout technique with lateral resolution is used on library in array format in which the position encodes the composition.

In our approach, the libraries are prepared onto conducting fluorine-doped tin oxide (FTO) by ink-jet printing (IJP) and electrodeposition made into the openings of an insulating mask. The mask serves to reduce the (capacitive and parasitic) background currents and enhances the sensitivity. Inks with defined salt concentrations and physical properties (viscosity, surface tension) were developed. We prepared arrays with defined mixing ratios of metal and a good positional accuracy.

The readout of the arrays was carried out by using the scanning photoelectrochemical microscopy (SPECM) [3,4,5]. In SPECM an optical fiber scans over the surface. Broadband laser light is coupled into the fiber with an inner core diameter of 105 µm to provide the illumination. Photoelectrochemcial reactions can happen at the illuminated parts of the substrates. This local photoelectrochemical reactions are measured via the integral substrate current i_S. Hence the 2D map of i_S vs. the fiber position (x,y) shows the photocurrent at each coordinate. The photocurrent is proportional to the photocatalytic activity, since every reacted H_2O molecule transfers 2 electrons to the surface of the substrate.

Literature:

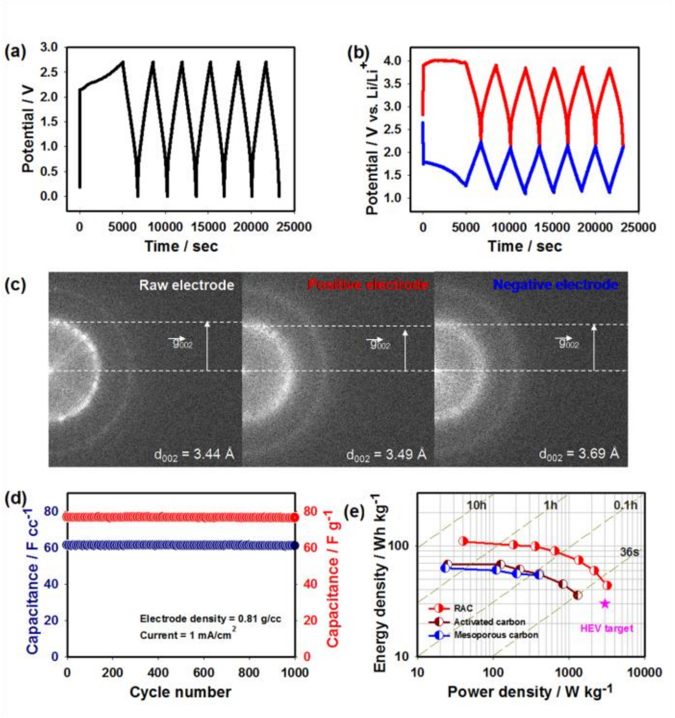
[1] V. S. Vidyarthi, M. Hofmann, A. Savan, K. Sliozberg, D. Koenig, R. Beranek, W. Schuhmann, A. Ludwig, *Int. J. Hydrogen Energy* **2011**, *36*, 4724. [2] S. P. Berglund, H. C. Lee, P. D. Nunez, A. J. Bard, C. B. Mullins, *Phys. Chem. Chem. Phys.* **2013**, *15*, 4554. [3] P. James, N. Casillas, W. H. Smyrl, *J. Electrochem. Soc.* **1996**, *143*, 3853-3865 [4] J. Lee, H. Ye, S. Pan, A. J. Bard, *Anal. Chem.* **2008**, *80*, 7445. [5] C. Bhattacharya, H. C. Lee, A. J. Bard, *J. Phys. Chem. C* **2013**, *117*, 9633.

Ribbon-like activated carbon with a multi-structure for supercapacitors

Mok-Hwa Kim,[ab] Kwang-Bum Kim,[b] Kisuk Kang,[c] Joong Tark Han,[d] Kwang Chul Roh[*a]

[a]*Energy & Environmental Division, Korea Institute of Ceramic Engineering & Technology, Seoul 153-801, Republic of Korea.*
[b]*Department of Materials Science & Engineering, Yonsei University, Seoul 120-749, Republic of Korea*
[c]*Department of Materials Science & Engineering, Seoul National University, Seoul 151-742, Republic of Korea*
[d]*Nano Carbon Materials Research Group, Korea Electrotechnology Research Institute, Changwon 642-120, Republic of Korea*
kitten0812@naver.com, rkc@kicet.re.kr

Ribbon-like activated carbon (RAC) has been successfully developed by a two-step activation process based on alkali activation and an electrochemical activation route. The multi-structure of the RAC features a porous graphitic structure with the coexistence of micropores and graphitic structures, mainly originating from the loose packing of the graphite sheets as a result of the degree of graphitization controlled by the carbonization conditions. RAC provides the tremendous benefits of excellent cycle life, high power (3.2 kW kg^{-1}), and high energy density (43.5 W h kg^{-1}) for electric double-layer capacitors, because of its graphitic architecture comprised of micropores and ring-shaped crystalline structures. In addition to investigating the improved electrochemical performance, we observed an interesting feature of the RAC: the obtained RAC has a high structural stability as shown by ex-situ high-resolution transmission electron microscopy (HR-TEM). These extraordinary results are attributed to the unique structure of RAC.

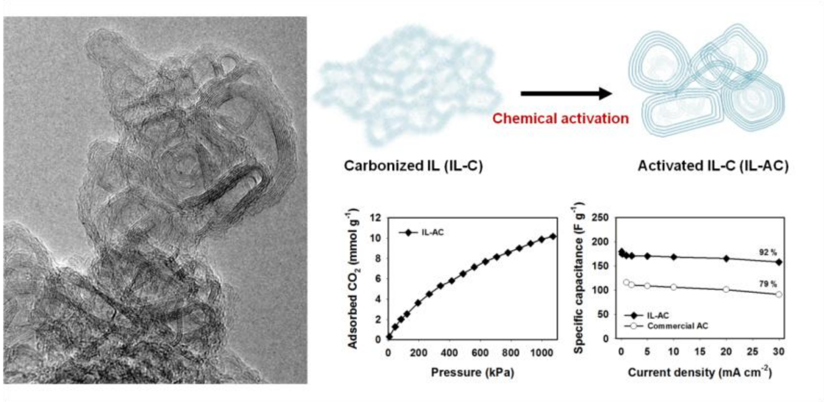


Retransformed graphitic activated carbon from ionic liquid-derived carbon containing nitrogen

Kwang Chul Roh[*a], Mok-Hwa Kim,[ab] Sol Yun,[d] Ho Seok Park,[*d] Joong Tark Han,[c] Kwang-Bum Kim[b]

[a]*Energy & Environmental Division, Korea Institute of Ceramic Engineering & Technology, Seoul 153-801, Republic of Korea.*
[b]*Department of Materials Science & Engineering, Yonsei University, Seoul 120-749, Republic of Korea*
[c]*Nano Carbon Materials Research Group, Korea Electrotechnology Research Institute, Changwon 642-120, Republic of Korea*
[d]*School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea.*
rkc@kicet.re.kr

Carbonization and chemical activation of an ionic liquid (EMIM–dca) are demonstrated to produce an outstanding structural combination of a high surface area through micro/mesopores and a graphitic structure that provides good electrical conductivity. These properties are attributed to the removal of nitrogen, which causes a rearrangement of atoms to create a new structure. To evaluate the potential of ionic liquid derived activated carbon (IL-AC) for use as an electrode material, it was used to assemble a two-electrode system for a supercapacitor. The rate performance was assessed through plots of specific capacitance versus current density for devices based on either IL-AC or commercial activated carbon. Note that despite this decrease in specific capacitance with increasing current density, 92% of the capacitance at 1.0 mA cm^{-2} is still retained at 30 mA cm^{-2}; a result which shows a consistently higher specific capacitance at increased current density than commercial activated carbon. This activated carbon has a very high CO_2 uptake and high specific capacitance, thus making it ideally suited to advanced energy storage systems.



Co-reactant Electrogenerated Chemiluminescece (ECL) from Carbon Dioxide in Ionic Liquids

David Bower, Conor F. Hogan
Dept. of Chemistry
La Trobe Institute for Molecular Science
La Trobe University, 3083, VIC, Australia
d.bower@latrobe.edu.au

Ionic liquids allow access to a variety of different electrochemical mechanisms that are not seen in traditional molecular solvents. When used as a thin layer on a screen printed electrode, ionic liquids allow rapid and responsive detection of carbon dioxide gas via electrogenerated chemiluminescence (ECL). While oxalate is typically produced by carbon dioxide reduction in traditional solvents, our studies suggest that the ECL emission produced in the ionic liquid arises as a result of the direct reduction of CO_2 to $CO_2^{\bullet-}$. This carbon dioxide radical anion is sufficiently stabilised to allow it to participate in the ECL reaction with a suitable species such as $Ru(bpy)_3^{3+}$.

Strong Catalytic Effect of Cobalt Oxide Nanoparticles on the Electrochemical Sensing of Arsenic

Cesar A. Barbero, Rusbel Coneo Rodriguez, Diego F. Acevedo, Gabriel A. Planes

Chemistry Department, National University of Rio Cuarto,
Ruta 8 km 601, 5800-Rio Cuarto, Argentina
cesarbarbero@gmail.com

Modified electrodes can be used for the electrochemical sensing of contaminant in aqueous environment. The usual modified electrode is made by covering a conducting material (e.g. glassy carbon) with a thin film of and catalytic layer. While cyclic voltammetry allows to qualitatively evaluating the catalytic effect of the layer, a quantitative analysis requires controlled mass transfer such that obtained using rotating disk electrodes.

Besides thin films, solid nanoparticles could be used as catalytic material for sensing contaminants. In that sense, so called “electrocatalytic” effects have been observed for electrodes modified with nanoparticles (e.g. carbon nanotubes). However, it has been shown that diffusion effects in the nanoparticle layer could be mistaken for changes in charge transfer rates.[1] Similar effects have been observed with porous electrodes.[2]

Recently, a quantitative model for the surface catalysis of nanoparticles modified electrodes, which take into account mass transfer effects have been proposed by Compton and coworkers.[3]

In the present communication we measure both cyclic voltammetry (CV) and rotating disk voltammetry (RDV) of arsenite oxidation on glassy carbon electrodes modified with cobalt oxide nanoparticles. The nanoparticles were deposited by cyclic voltammetry of the base electrode in cobalt (II) solution,[4] allowing to control the amount of material deposited on the surface. The redox properties of the cobalt oxide nanoparticles are measured by cyclic voltammetry while the ion exchange is measured by Probe Beam Deflection (PBD).[4]

Both CV and RDV show a strong effect of the amount of nanoparticles on the apparent overpotential for arsenite oxidation. The model proposed by Compton and coworkers,[3] is modified assuming that the cobalt oxide nanoparticles acts as volumetric redox catalysts and not only as surface catalysts.

The effective charge transfer constant shifts with the amount of nanoparticles in a way that corresponds to the modified model.

The relevance of the data for the design of electrochemical sensors for arsenic species is discussed.

Acknowledgements
C.A.B and G.A.P are research fellows of CONICET. A.B.M and R.C.R thank CONICET for graduate fellowships. The authors wish to thank the EU (IRSES project ‘‘SUMA2-Network’’, Pr. No: 318903) for the financial support for the scientist’s mobility.

References
[1] D.F. Acevedo, S. Reisberg, B. Piro, D.O. Peralta, M.C. Miras, M.C. Pham, C.A. Barbero, *Electrochimica Acta,* 53 (2008) 4001–4006
[2] R. Coneo Rodriguez, A. Baena Moncada, D.F. Acevedo, G.A. Planes, M.C. Miras, Cesar A. Barbero, *Faraday Discuss.* 164(2013)147-173
[3] J Masa, C Batchelor-McAuley, W Schuhmann, RG Compton, *Nano Research*, 7(2014)71-78.
[4] C.Barbero, G.A. Planes, M.C. Miras, *Electrochemistry Communications*, 3(2001)113

operando synchrotron X-ray analysis of lithium ion cathode reaction

Yoshiharu Uchimoto and Yuki Orikasa
Graduate School of Human and Environmental Studies, Kyoto University,
Yoshida, Kyoto 606-8510, Japan
Uchimoto.yoshiharu.2n@kyoto-u.ac.jp

operando analysis enables us to observe dynamic behavior occurring in an operating battery without touching its components and so actual processes associated with charging/discharging can be elucidated. The difficulty in in situ analysis has been low time resolutions. Recently the measuring probes have been much improved and observation at practical charging/discharging rate to 50 C is now available. In this study, operando techniques by using synchrotron X-ray method and its application to lithium battery analysis using their measurement characteristics are demonstrated.

1. Snapshot Observation of Phase Transition Dynamics in $LiFePO_4$ [1-2]

operando analysis enables us to observe dynamic behavior occurring in an operating battery without touching its components and so actual processes associated with charging/discharging can be elucidated. The difficulty in in situ analysis has been low time resolutions. Recently the measuring probes have been much improved and observation at practical charging/discharging rate to 50 C is now available. In this study, in situ techniques by using synchrotron X-ray method and its application to lithium battery analysis using their measurement characteristics are demonstrated.

For $LiFePO_4$ electrodes, we tracked the phase transition behavior under 1C rate charging conditions and figured out that there are various intermediate states between the LFP (discharged) and FP (charged) phases that have not been clarified with ex situ analysis. The smaller the particle size was, the greater the intermediate states changes until it reached to the thermodynamically stable FP phase. At much higher rate of 10 C, we found a new metastable crystalline phase "Li_xFP". This result shows that such a metastable phase can be a kinetically favorable intermediate when a strong motive force (large polarization) exists.

2. operando X-ray Absorption Spectroscopic Study on Stability at Electrode / Electrolyte Interface [3-5]

Lithium-ion batteries (LIBs) have been used as power sources for mobile devices such as cell phones and mobile PCs because of their large energy densities. In order to enhance LIB performance, it is very important to understand the electrode/electrolyte interface reactions because these reactions greatly affect the cyclability and power density of LIB. However, the mechanisms of such interface reactions have not yet been fully understood due to the difficulty of their direct observation for the reactions at nanoscale. Our group has directly observed the interface reactions of a thin-film model electrode of $LiCoO_2$ by in-situ total-reflection fluorescence X-ray absorption spectroscopy (in-situ TRF-XAS). As a result, we clarified that irreversible change occurred at the surface of $LiCoO_2$ during the charge/discharge process: the change is related to the degradation of $LiCoO_2$ electrode. $LiFePO_4$ shows higher cyclability in terms of capacity during the charge/discharge process than $LiCoO_2$. A higher degree of reversibility of the electronic states at the surface of $LiFePO_4$ is expected during the charge/discharge process. In this work, we have investigated the reversibility of the surface of a $LiFePO_4$ thin-film electrode by using in-situ TRF-XAS.

References

1) Y. Orikasa, T. Maeda, Y. Koyama, H. Murayama, K. Fukuda, H. Tanida, H. Arai, E. Matsubara, Y. Uchimoto, Z. Ogumi, *Chem. Mater*., 2013, 25, 1032 – 1039

2) Y. Orikasa, T. Maeda, Y. Koyama, H. Murayama, K. Fukuda, H. Tanida, H. Arai, E. Matsubara, Y. Uchimoto, Z. Ogumi, *J. Am. Chem. Soc.*, 2013, 135, 5497 – 5500

3) Yuki Orikasa, Daiko Takamatsu, Kentaro Yamamoto, Yukinori Koyama, Shinichiro Mori, Titus Masese, Takuya Mori, Taketoshi Minato, Hajime Tanida, Tomoya Uruga, Zempachi Ogumi and Yoshiharu Uchimoto *Adv. Mater. Interface*, 2014, 1, 1400195

4) Kentaro Yamamoto , Taketoshi Minato, Shinichiro Mori, Daiko Takamatsu, Yuki Orikasa, Hajime Tanida, Koji Nakanishi, Haruno Murayama, Titus Masese, Takuya Mori, Hajime Arai, Yukinori Koyama, Zempachi Ogumi, Yoshiharu Uchimoto, *J. Phys. Chem. C*, 2014, 118, 18, 9538 – 9543

5) D. Takamatsu, Y. Koyama, Y. Orikasa, S. Mori, T. Nakatsutsumi, T. Hirano, H. Tanida, H. Arai, Y. Uchimoto, Z. Ogumi, *Angewandte Chemie. Int. Ed.*, 2012, 51, 11597 – 11601

Complex Electrochemical Detection of Damage to DNA Using Simple Label-Free DNA Biosensors

Vlastimil Vyskočil[1], Andrea Hájková[1], Marta Blašková[1], Zuzana Jurečková[1], Christian Iffelsberger[2], and Frank-Michael Matysik[2]

[1] Charles University in Prague, Faculty of Science, University Research Centre UNCE "Supramolecular Chemistry", Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Hlavova 2030/8, 12843 Prague 2, Czech Republic,
e-mail: vlastimil.vyskocil@natur.cuni.cz

[2] University of Regensburg, Faculty of Chemistry and Pharmacy, Institute of Analytical Chemistry, Chemo- and Biosensors, Universitätsstraße 31, 93040 Regensburg, Germany,
e-mail: frank-michael.matysik@chemie.uni-regensburg.de

A complex diagnostic approach in the detection of DNA damage represents a novel model for *in vitro* classification of potentially genotoxic chemical (environmental pollutants, pesticides, conventional or newly synthesized drugs, *etc.*) or physical (UV radiation, gamma radiation, *etc.*) agents. It is based on a set of criteria that determine whether and under which conditions the investigated agent causes damage to DNA. In this model, a diagnostic tool used to collect data is represented by an electrochemical DNA biosensor and an appropriate electrochemical detection technique [1]. Such DNA biosensors are designed with a special emphasis on their high efficiency and, at the same time, on their simple, fast, and inexpensive fabrication.

In our UNESCO Laboratory of Environmental Electrochemistry, we developed two prototypes of DNA biosensors suitable for the complex electrochemical detection of damage to DNA: (i) a glassy carbon electrode and (ii) a microcrystalline natural graphite–polystyrene composite film electrode, both modified with low molecular weight double-stranded DNA from salmon sperm immobilized onto the electrode surface as a biorecognition layer [2,3]. A complex characterization of a specific damaging event is then obtained using a combination of several electrochemical detection techniques (*e.g.*, cyclic voltammetry, differential pulse voltammetry, square-wave voltammetry, and electrochemical impedance spectroscopy) [1–3].

In this contribution, fundamental ideas of this diagnostic approach will be introduced and practically demonstrated on two selected xenobiotic compounds: (i) 2-aminoanthracene (a well-known hazardous substance exhibiting genotoxic effects [4]) and (ii) hydroxyl radicals (well-known reactive oxygen species inducing the oxidative stress in DNA [1], which are generated for our purposes either chemically by the Fenton reaction or electrochemically on the surface of boron-doped diamond film electrodes or lead dioxide film electrodes).

V.V. thanks the Grant Agency of the Czech Republic (Project GP13-23337P) and A.H., M.B., and Z.J. thank the Grant Agency of the Charles University in Prague (Project GAUK 430214/2014/B-CH/PrF) for the financial support.

References

1. L. Hlavata, K. Benikova, V. Vyskocil, J. Labuda, Electrochim. Acta 71 (2012) 134–139.
2. A. Hajkova, J. Barek, V. Vyskocil, Electroanalysis 27 (2015) 101–110.
3. V. Vyskocil, J. Barek, Procedia Chem. 6 (2012) 52–59.
4. K. Jemnitz, Z. Veres, G. Torok, E. Toth, L. Vereczkey, Mutagenesis 19 (2004) 245–250.

The Oxidation Processes of Benzylaminopurines at Pencil Graphite Electrodes Modified by Monovalent Copper Ions

Iveta Pilarova[1], Ondrej Laskafeld[1], Premysl Lubal[1, 2] and Libuse Trnkova[1, 3]*
[1] *Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, CZ – 625 00 Brno, Czech Republic; 175126@mail.muni.cz*
[2] *CEITEC MU, Zerotinovo namesti 617/9, CZ – 601 77 Brno, Czech Republic*
[3] *CEITEC, University of Technology, Technicka 3058/10, CZ – 616 00 Brno, Czech Republic; *libuse@chemi.muni.cz*

Benzylaminopurine (6-BAP), the most important cytokinin of adenine type [1], and its methoxylated and chlorinated derivatives in the form of dinuclear complexes with metal ions [2,3] are a hot topic in biomedicine. BAPs are investigated as possible enzyme inhibitors, anti-bacterial, anti-viral and anti-tumor agents [4-7]. The theoretical investigations of some 6-benzylaminopurine derivatives together with X-ray, FT-IR and Raman spectroscopy characterization were performed by Cajan et al. [8].

The aim of our contribution is the systematic voltammetry study of the oxidation processes of methoxylated and chlorinated (in positions 2', 3' and 4' of benzene ring) derivatives of 6-BAP. Voltammetric studies using LSV and CV techniques were performed in buffered H_2O/CH_3OH solutions (pH 3.18 – 6.8; 2% v/v of CH_3OH) utilizing a pencil graphite electrode (PeGE-Tombow, Japan), the surface of which was *in-situ* modified with monovalent copper.

The sensing is based on the formation of Cu(I)-BAP surface complexes which are subsequently stripped out from the electrode by potential scan. The stripping mode enables higher sensitivity in detecting the oxidation signals of all BAP derivatives. Where appropriate, voltammetric data were treated with Elimination voltammetric procedure – EVP [9-12] to obtain details of the studied electrochemical transformations. The electrochemical experiments were complemented with UV/VIS spectral experiments, electron densities on atoms and precise determinations of the HOMO levels of the studied purine derivatives were obtained by quantum chemistry calculations.

Acknowledgement

This research has been supported by projects: MUNI/A/0972/2013 and MUNI/A/1452/2014 ; KONTAKT II (LH 13053) project of the MEYS of the Czech Republic; CEITEC CZ.1.05/1.1.00/02.0068 and SIX CZ.1.05/2.1.00/03.0072. The authors are grateful to Professor Zdenek Travnicek (Faculty of Inorganic Chemistry, Palacky University in Olomouc) for providing derivatives of 6-BAP.

References

[1] P. Tarkowski, K. Dolezal, M. Strnad, Chemicke Listy (eng.), 98 (2004) 834-841.
[2] M. Malon, Z. Travnicek, M. Marysko, et al., Transition Metal Chemistry, 27 (2002) 580-586.
[3] Z. Travnicek, L. Szucova, I. Popa, Journal of Inorganic Biochemistry, 101 (2007) 477-492.
[4] A.Y. Louie, T. J. Meade, Chemical Reviews, 99 (1999) 2711-2734.
[5] H. Sigel, Chemical Society Reviews, 33 (2004) 191-200.
[6] H. H. Hammud, G. Nemer, W. Sawma, et al., Chemico-Biological Interactions, 173 (2008) 84-96.
[7] P. Starha, Z. Travnicek, R. Herchel, et al., Journal of Inorganic Biochemistry, 103 (2009) 432-440.
[8] M. Cajan, Z. Travnicek, J. Mol. Struct., 994 (2011) 350-359.
[9] L.Trnkova, Application of elimination voltammetry with linear scan in biochemistry. In *Utilizing of Bio-Electrochemical and Mathematical Methods in Biological Research,* Adam, V.; Kizek, R., Eds. Research Signpost: Kerala, India, 2007; Chapter 4, pp 51-74.
[10] N. Serrano, A. Alberich, L. Trnkova, Electroanalysis, 24 (2012) 955-960.
[11] N. Aladag, L. Trnkova, A. Kourilova, M. Ozsoz, F. Jelen, Electroanalysis, 22 (2010) 1675-1681.
[12] R. Navratil, F. Jelen, Y.U. Kayran, L. Trnkova, Electroanalysis, 26 (2014) 952-961.

Study of the stability of the passive film formed on copper-based binary alloys in 3% NaCl solution

L. Babouri*[1], K. Belmokre[2], Y. El Mendili[3], A. Abdelouas[3], A.Kabir[2]

[1] *Ecole Normale Supérieure d'Enseignement Technologique de Skikda, Algérie*
[2] *Departement des sciences de la matière, Université du 20 aout 1955-Skikda, Algérie*
[3]*Laboratoire SUBATECH, CNRS-IN2P3, Ecole des Mines de Nantes-Université de Nantes, 4 rue Alfred Kastler, BP 20722, 44307 Nantes cedex 03, France.*

E-mail address: l.babouri@yahoo.fr
Tel.: +213(0)770974775.

Abstract

The interaction of copper-based binary alloys with aggressive environment results in the formation of a passive and adhering film which protects the metal surface by limiting the ion transport toward the aggressive environment.

The present work aims to contribute to the identification of the nature of the films formed on the surface of two copper-based binary alloys (Cu70Ni30 and Cu77Zn21) at open circuit potential in 3% NaCl and to study the effect of some experimental factors (the concentration of chloride, the temperature, the agitation and the PH) on the stability of the formed film.

This study was conducted, in 3% NaCl aggressive environment, with electrochemical tests, weight loss measures associated to the atomic absorption spectroscopy technique (AAS). The observation of the surface state of the two alloys was done by means of SEM coupled to EDX techniques. The assessment of the stability of the formed passive films was based on the extent passivation level calculated from the obtained electrochemical parameters.

The results show that the formed passive films, at free potential, contained Cu_2O, CuO and ZnO for the Cu-Zn alloy while for the Cu-Ni alloy, the formed passive film was found to be composed of Cu_2O, CuO and NiO. The influence of experimental factors on the stability of the passive films was set in evidence.

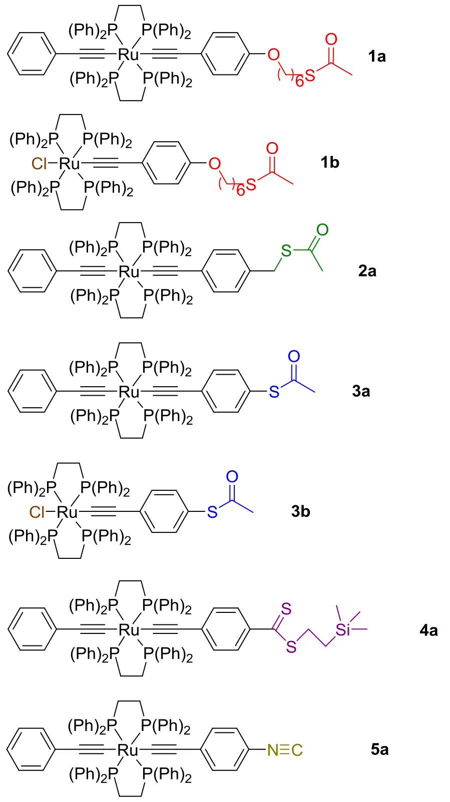
Keywords: *copper alloys; NaCl3% ; passive film ; electrochemical techniques ; physical methods.*

Fast Redox Communication at Acetylides – Ruthenium thiols, dithiocarboxylic acid and isocyanide SAMs on gold

Corinne Lagrost, Andrea Mulas, Yves-Marie Hervault, Xiaoyan He, Lucie Norel, Stéphane Rigaut
Institut des Sciences Chimiques de Rennes UMR CNRS n°6226
Université de Rennes 1 -Campus de Beaulieu, F-35042 Rennes Cedex, France
Corinne.lagrost@univ-rennes1.fr

Controlled modification of conducting surfaces at the molecular level with redox-active building blocks is an efficient approach to design integrated devices for data storage and transfer. Different redox-active carbon rich group 8 σ-alkynyl complexes have been emerged as potential candidates for reversible charge storage systems at the molecular level.[1] Carbon-rich ruthenium complexes are used to form Self-Assembled Monolayers (SAMs) onto gold surfaces using different anchoring groups, thiols, dithiocarboxylic acid and isocyanide. These organometallic compounds promote a strong electronic coupling between the metal centers and the conjugated organic ligands so they exhibit fast electron transfer rates combined to low oxidation potentials.[1,2] These properties are highly desirable for developing electrochemically switchable devices exhibiting fast clocking rates, since the electron-transfer through gold-SAMs hybrid interfaces is the factor determining the macroscopic "response time" thus efficiency for any devices using these junctions as component memory elements.

Herein, we report the preparation and characterization of the different Ruthenium-acetylides SAMs. Electron transfer kinetics within the SAMs was examined using fast cyclic voltametry.



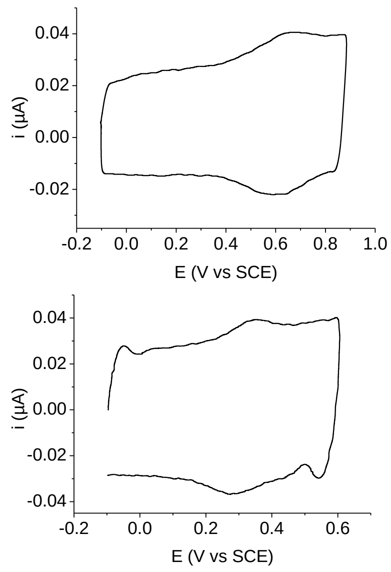


Figure: **left**, structure of the acetylides-Ru. **Right**, Cyclic voltammetry of SAMs at gold surface with (bottom) complex 4a (10 µm electrode, 10 kV/s) and (top) complex 2a (10 µm electrode, 10 kV/s)

---

[1] (a) Liu, Y.; Lagrost, C.; Costuas, K.; Tchouar, N.; Bozec, H.; Rigaut, S., *Chem. Commun.* **2008**, 6117-6119. (b) Liu, Y. ; Ndiaye, C. M. ; Lagrost, C ; Costuas, K ; Choua, S ; Turek, P.; Norel, L.; Rigaut, S. *Inorg. Chem.*, **2014**, 53, 8172-8188. (c) Halet, J.F.; Lapinte, C.; *Coord. Chem. Rev.*, 2013, 257, 1584-1613

[2] Meng, F.; Hervault, Y.-M.; Shao, Q.; Hu, B.; Norel, L.; Rigaut, S.; Chen, X. *Nat. Commun.* DOI: 10.1038/ncomms4023

Non-covalent interactions in water electrolysis: influence on the activity of Pt(111) and iridium oxide catalysts in acidic media

Alberto Ganassin [a], Viktor Colic [b], Jakub Tymoczko [a], Aliaksandr S. Bandarenka[b],
Wolfgang Schuhmann [a]

[a] Analytical Chemistry - Center for Electrochemical Sciences (CES); Ruhr-Universität Bochum,
Universitätsstr. 150, 44780 Bochum; Germany
[b] Physik-Department ECS, Technische Universität München, James-Franck-Straße 1,
85748 Garching; Germany
e-mail: alberto.ganassin@rub.de

Electrolyte components which are typically not considered to be directly involved in catalytic processes at solid-liquid electrified interfaces often demonstrate significant or even drastic influence on the activity, stability and selectivity of electrocatalysts. While there has been certain progress in the understanding of these electrolyte effects, lack of experimental data for various important systems frequently complicates a rational design of new active materials.

Modern proton-exchange membrane (PEM) electrolyzers utilize Pt- and Ir-based electrocatalysts which are among the very few materials which are both active and stable under the extreme conditions of water splitting. We use model Pt(111) and Ir-oxide films grown on Ir(111) electrodes and explore the effect of alkali metal cations and sulfate-anions on the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) in acidic media. We demonstrate that perchlorate and sulfate anions have an impact on the oxidation process of Ir(111) and on the OER at anodically grown Iridium oxide while Rb^+ drastically promotes the HER at Pt(111) electrodes as compared to experiments performed in the reference electrolyte $HClO_4$. Specific adsorption of sulfate ions on Ir(111) hinders the oxidation of the metallic surface thus shifting the reaction to more positive potentials. Sulfates also decrease the activity towards OER if compared to the reaction performed in a solution containing non-specifically adsorbed perchlorate anion. Alkali metal cations do influence HER and HOR on Pt(111) surfaces. In particular HER and HOR activities in Rb^+ ions containing electrolytes at a Pt(111) electrode are almost the same as the activities at the polycrystalline Pt electrode.

To underline the particular importance of the electrode/electrolyte interface properties, one can note as a methodological issue that solutions of $HClO_4$ are often used as model electrolytes in electrocatalysis because of their presumably weak interaction with the electrode surface. However, in the case of PEM electrolyzers $HClO_4$ is not the most relevant medium, and the extensive use of Nafion® as proton-conducting membrane imposes questions about the influence of sulfonate groups on the efficiency of the system. In fact, the adsorption of sulfates plays an important role concerning the electrocatalytic properties.

Acknowledgement: Financial support from the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Imaging of Concentration Distributions on Corroding Magnesium Exposed to Aqueous Environments using Scanning Electrochemical Microscopy

J. Izquierdo[a], B.M. Fernández-Pérez[a], J.J. Santana [b], R.M. Souto[a]
[a]*Department of Chemistry, University of La Laguna, P.O. Box 456, E-38200 La Laguna (Tenerife, Canary Islands), Spain*
rsouto@ull.es
[b]*Department of Process Engineering, University of Las Palmas de Gran Canaria, E-35017 Las Palmas de Gran Canaria (Gran Canaria, Canary Islands), Spain*

Magnesium and its alloys have a great potential for several industrial and biomedical applications due to their non-toxicity and high strength-weight ratio, though their practical use is greatly limited by their poor corrosion resistance in most aqueous environments. In order to slow down this degradation, it is mandatory to gather precise knowledge about the mechanism of the process. Unfortunately, the mechanism of magnesium corrosion remains mostly unknown or at least controversial, and it presents certain singular features when compared to the corrosion of other active metals. Thus, the main cathodic half-reaction leads to hydrogen evolution, but this reaction has been recorded to occur on magnesium not only under cathodic polarization as expected, but also when increasing anodic overpotentials are applied to the material. This phenomenon, widely termed as the "Negative Difference Effect" [1,2], has been traditionally invoked to support the formation of magnesium(I) cations as intermediate species during the degradation of this metal [1]. That is, oxidation of magnesium at the anodic sites would produce Mg(I) species which subsequently react with water producing the hydrogen gas [1,3]. However, the use of a new range of sensitive microelectrochemical and spectroelectrochemical methods are delivering new experimental evidences that anodic dissolution is Mg(II) instead [4-8], whereas some of the processes involved in the experiments traditionally considered to prove the existence of Mg(I) some decades ago [9] may have been possibly misunderstood [10]. Therefore, the actual mechanism is still to be established unambiguously, which is required if an effective control of the corrosion process to be gained for the application of magnesium-based materials in practical situations.

The Scanning Electrochemical Microscopy (SECM) is presented here as an essential tool for the local characterization of the still uncertain mechanism for magnesium corrosion. The reaction leading to hydrogen evolution from separated magnesium cathodes and anodes has been imaged using appropriate operation modes for the SECM. Antimony microelectrodes permitted to follow the pH gradients resulting from the water electrolysis, whereas platinum microdisks were used to amperometrically determine the subsequent local evolution of hydrogen. Evidences of alkalization and H_2 production were found over the magnesium cathode, whereas exclusively some minor local acidification was observed above the anode. Next, by using ion-selective microelectrodes as probes, the concentration distribution of dissolving Mg^{2+} ions was imaged with high spatial resolution.

References:

[1] G. Song, Adv. Eng. Mater. 7 (2005) 563.
[2] E. Ghali, W. Dietzel, K.-U. Kainer, J. Mater. Eng. Perform. 22 (2013) 2875.
[3] Z. Qiao, S. Shi, N. Hort, N.I.Z. Abiding, A. Atrens, Corros. Sci. 61 (2012) 185.
[4] G. Williams, H.N. McMurray, J. Electrochem. Soc. 155 (2008) C340.
[5] J. Świątowska, P. Volovitch, K. Ogle, Corros. Sci. 52 (2010) 2372.
[6] N.T. Kirkland, G. Williams, N. Birbilis, Corros. Sci. 65 (2012) 5.
[7] J. Izquierdo, L. Nagy, I. Bitter, R.M. Souto, G. Nagy, Electrochim. Acta 87 (2013) 283.
[8] G. Williams, H. ap Ll. Dafydd, R. Grace, Electrochim. Acta 109 (2013) 489.
[9] R.I. Petty, A.W. Davidson, J. Kleinberg, J. Amer. Chem. Soc. 76 (1954) 363.
[10] A. Samaniego, B.L. Hurley, G.S. Frankel, J. Electroanal. Chem. (2015) in press, http://dx.doi.org/10.1016/j.elechem.2014.04.013.

Corrosion resistance of new ternary Ti-Ta-Zr alloy in artificial saliva simulating severe functional conditions

C. Vasilescu, S. I. Drob, P. Osiceanu, J. M. Calderon Moreno
Institute of Physical Chemistry, 202 Spl. Independentei, 060021, Bucharest, Romania
Email address: cora_vasilescu@yaho.com

A new Ti-15Ta-5Zr alloy with low density, proper elastic modulus and, suitable mechanical properties was elaborated. Both optical and scanning electron (SEM) micrographs revealed a homogeneous bi-phase $\alpha + \beta$ microstructure with lamellas of α and β phases. This very homogeneous microstructure assures high corrosion stability of the alloy.

The alloy native passive film comprises both Ti_2O_3 and TiO_2 oxides and very resistant Ta_2O_5 and ZrO_2 oxides (X-ray photoelectron spectroscopy-XPS). The thickness of this native passive film was .5 nm, a thick film that can provide superior protection to substrate.

Corrosion resistance of this alloy in severe functional conditions, in artificial Carter-Brugirard saliva of different pH values and content (without and with NaF) was studied. All main electrochemical and corrosion parameters had more favourable values than those of Ti, due to Ta and Zr alloying elements, which contributed with their protective oxides to the passive native layer and due to the alloy very homogeneous microstructure. The corrosion current densities decreased of about 6-22 times for alloy comparing with Ti, as result of the alloy more resistant passive film; correspondingly, the total quantity of ions released into Carter-Brugirard saliva was very low, i.e., Ti-15Ta-5Zr alloy has a much reduced toxicity. The polarisation resistances had higher values for the alloy in comparison with Ti, proving more protective passive film. The acid, alkaline and existence of F^- ions in Carter-Brugirard saliva conducted to the slightly more unfavourable values of all above mentioned parameters because of the interactions of saliva with the passive layer; however, the alloy remained “Perfect Stable” in these environments, denoting a very stable, resistant, protective passive layer on its surface.

Nyquist and Bode impedance spectra indicated a passive film formed by two layers: an inner, insulating, barrier layer that provides the high corrosion resistance and an outer, porous layer that permits the absorption of ions and species from surrounding environment into its pores, favouring both dissolution and absorption processes, namely, interactions and bioactivity.

The increase of the alloy open circuit potentials in time shows that its passive film is resistant to the attack of the aggressive ions from Carter-Brugirard saliva and thickens over time. These facts were confirmed by XPS analysis and SEM observations, which detected new depositions of 5 nm thickness on the alloy surface after 500 immersion hours in Carter-Brugirard saliva; this new layer contains Na_3PO_4 and K_3PO_4 protective compounds, which confer both corrosion resistance and bioactivity to the substrate. Therefore, the new Ti-15Ta-5Zr alloy is a promising material for dental implant.

Local electrochemical impedance spectroscopy applied to the corrosion protection of waterborne coatings on a 2024 aluminium alloy

Anh Son Nguyen, Nadine Pébère
Université de Toulouse, CIRIMAT, UPS/INPT/CNRS
ENSIACET, 4 Allée Emile Monso – CS 44362, 31030 Toulouse, France
anhson.nguyen@ensiacet.fr

Abstract

The organic coatings currently used in the aerospace industry present very high corrosion protection. However, since the beginning of the 1990s, the high toxicity associated with Cr(VI) has imposed restrictions on their use in industrial applications and particularly in organic coatings. Today, the replacement of chromates remains an important challenge and, during the last decades, numerous works were devoted to the incorporation of "green" corrosion inhibitors in coatings to provide an active corrosion protection [1-4].

The major purpose of the present work is to contribute to a better understanding of the local corrosion inhibition mechanisms by using local electrochemical impedance spectroscopy (LEIS) in the presence and absence of an artificial defect in the coatings. Two commercial coatings (epoxy-polyamido amine waterborne paint) with and without chromates deposited on a 2024 aluminium alloy were characterized. The waterborne system containing chromates constitutes the reference.

In a previous work [5], the global impedance responses of the same coatings were characterized in dry and wet conditions. It was shown that the barrier properties of the two coatings were good. The impedance data analysis suggested that water penetration occurred on a shorter time scale than ionic penetration.

Local electrochemical measurements performed on intact coatings corroborated the global impedance behaviour whereas LEIS on scratched samples allowed the release of inhibitors and the self-healing properties of the coatings to be validated. Understanding of fundamental protection mechanisms remains to be elucidated with additional local impedance diagrams analysis. This work is in progress.

References

[1] M.L. Zheludkevich, S.K. Poznyak, L.M. Rodrigues, D. Raps, T. Hack, L.F. Dick, T. Nunes, M.G.S. Ferreira, Corros. Sci. 52 (2010) 602-611.
[2] D. Snihirova, S.V. Lamaka, M.F. Montemor, Electrochim. Acta, 83 (2012) 439-447.
[3] I.A. Kartsonakis, E. Athanasopoulou, D. Snihirowa, B. Martins, M.A. Koklioti, M.F. Montemor, G. Kordas, C.A. Charitidis, Corros. Sci. 85 (2014) 147-159.
[4] D. Snihirova, S.V. Lamaka, M.M. Cardoso, J.A.D. Condeço, H.E.C.S. Ferreira, M.F. Montemor, Electrochim. Acta, 145 (2014) 123-131.
[5] A.S. Nguyen, M. Musiani, M.E. Orazem, N. Pébère, B. Tribollet, V. Vivier, Accepted for publication in Electrochim. Acta.

Acknowledgments
The authors gratefully acknowledge the Company MAPAERO (Pamiers, France) for the preparation of the coated samples and more particularly Pauline Côte and Pierre-Jean Lathière for fruitful discussion on coating technologies. The PhD thesis of Nguyen Anh Son is prepared in the framework of the associated international laboratory "Functional Composite Material (FOCOMAT)" between France and Vietnam.

Thin layer disposable flow cells as electrochemical detectors in FIA system.

L. Fernández-Llano, P. Fanjul-Bolado, D. Hernández-Santos, M.B. González-García
DropSens, S.L.
Edif. CEEI, Parque Tecnológico de Asturias, 33428, Llanera (Spain)
lfernandez@dropsens.com

Flow injection analysis (FIA) is a well-known technique with defined principles of operation. Flow-cells for screen-printed electrodes are usually wall-jet type. Here we propose an original thin layer flow-cell where channel slide is directly mounted over the screen-printed electrodes platform. The injection is done through an “in-line luer injection port” where sample volume can be easily controlled by operator through a syringe. This new configuration simplifies operability and effectiveness in working with FIA systems. The main advantages are: an easy and quick changing of electrode, a great decrease in air-bubble formation, a simple and easy method to change the sample volume injected, besides the typical advantages of FIA methodology. Moreover, the electrode configuration can be easily customized.

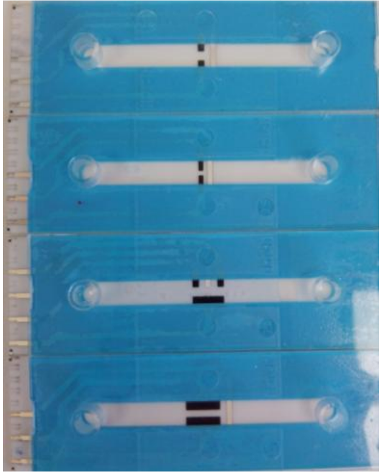


Figure 1. Integrated screen-printed electrodes in flow cell.

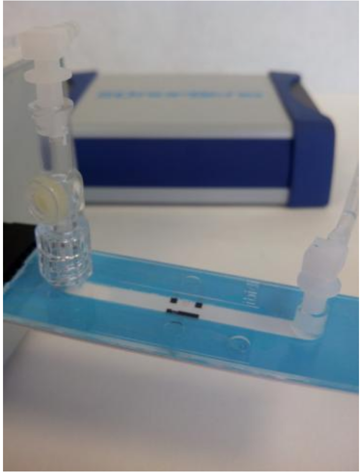


Figure 2. Integrated SPE-flow-cell in FIA system.

These different configurations have been successfully tested for paracetamol quantification, with high reproducibility between measurements and good correlation coefficients of calibration plots. Two working electrodes configuration is very promising for simultaneous detection of different species.

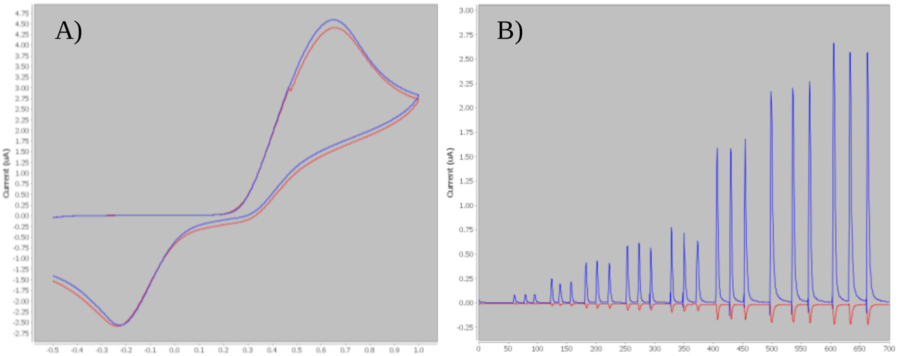


Figure 3. A) Cyclic voltamperogram $1x10^{-3}$M paracetamol in a two working electrodes flow-cell in Tris-NO_3 0.1M pH 10. B) Simultaneous amperometric detection of paracetamol at +0.6V (blue) and at -0.3V (red) in a two working electrodes flow-cell, in Tris-NO_3 0.1M pH 10; Flow rate=2,6mL/min.

[1]P. Fanjul-Bolado, P. J. Lamas-Ardisana, D. Hernández-Santos, A. Costa-García. Anal. Chim. Acta 638 (2009) 133-138

Extended-gate field-effect transistor (EG-FET) as the transducer in a chemosensor for stereoselective D- and L-phenylalanine determination

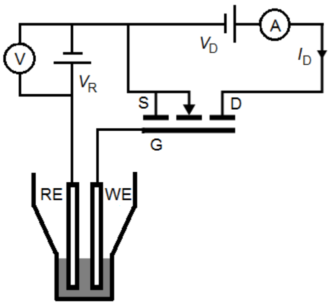
Zofia Iskierko[1], Anna Checinska[1,2], Piyush Sindhu Sharma[1], Krzysztof Noworyta[1], Krzysztof Fronc[3],
Wlodzimierz Kutner[1,4]

[1]Institute of Physical Chemistry of the Polish Academy of Sciences, 44/52 Kasprzaka, 01-224 Warsaw, Poland
[2]Department of Chemistry, Warsaw University of Technology, Plac Politechniki 1, 00-661 Warsaw, Poland
[3]Institute of Physics of the Polish Academy of Sciences, 32/46 Al. Lotników, 02-668 Warsaw, Poland
[4]Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszynski University in Warsaw, Dewajtis 5, 01-815 Warsaw, Poland

E-mail address: ziskierko@ichf.edu.pl

An extended-gate field-effect transistor (EG-FET) system was designed to isolate an FET from the chemical environment.[1,2] In this system, chemically recognizing unit was deposited on the surface of the gate extended from the FET.[3] The experimental setup prepared that way showed major advantage of flexibility in the gate shape.

Molecular recognition, especially steroselective recognition, is one of the most significant processes in diverse chemical and biological phenomena. The study of synthetic recognition systems for chiral recognition of amino acids is a field of increasing research activity. For instance, phenylalanine, similarly as other amino acids, is present in human body exclusively as an L-enantiomer. Even though L-enantiomers are equally stable as their respective D-counterparts, L-amino acids are the naturally preferable enantiomers. Specifically, proteins composed of L-amino acids interact with certain L-amino acids but not eagerly with their D-forms. If D-amino acids appear, even at low concentrations, in humans, then some antagonistic biological functions may occur.[4] Although literature[5] brings several examples of stereoselective recognition of phenylalanine, it is important to improve its enantioselective determination and develop similar determination methods for other chiral compounds.



Scheme 1. Experimental setup based on the EG-FET design, using a gold plate coated with the D- or L-phenylalanine-templated MIP as the gate (working electrode, **WE**), and a Pt wire as the reference electrode (**RE**). **G**, **D**, and **S** stand for the gate, drain, and source components of the FET structure, respectively. V_D, I_D, and V_R stand for the drain voltage, drain current and the reference voltage, respectively.

Molecular imprinting is a well-established procedure for preparing artificial recognition units of chemical sensors. Generally, it involves polymerization of functional monomers with cross-linking monomers in the presence of a template, which is most often the analyte itself. Subsequent removal of the template leaves in the polymer complementary cavities similar in their size, shape, and orientation of recognition sites to those of the template molecules.

Towards that, we have developed in the present study steroselective sensing systems for L- and D-phenylalanine by using molecularly imprinted polymers (MIPs) as recognition units. The MIP films were deposited by potentiodynamic electrochemical polymerization of the tailor designed *bis*(bithiophene) based functional monomers in the presence of the L- or D-phenylalanine template on the surface of an extended gate of a commercially available MOSFET (Scheme 1). The template removal was confirmed with the UV-vis spectroscopy and electrochemical measurements. Subsequently, the film was characterized by spectroscopic techniques as well as its morphology and thickness were determined by the AFM and SEM imaging. Then, binding of the phenylalanine enantiomers by their molecular cavities was detected with the EG-FET transducers. The devised chemosensors were then used for discrimination of L- and D-phenylalanine.

References
[1] C.-P. Chen, A. Ganguly, C.-Y. Lu, T.-Y. Chen, C.-C. Kuo, R.-S. Chen, W.-H. Tu, W. B. Fischer, K.-H. Chen, L.-C. Chen, *Anal. Chem.* **2011**, *83*, 1938–1943.
[2] P. D. Batista, M. Mulato, C. F. d. O. Graeff, F. J. R. Fernandez, F. d. C. Marques, *Braz. J. Phys.* **2006**, *36*, 478-481.
[3] L.-L. Chi, J.-C. Chou, W.-Y. Chung, T.-P. Sun, S.-K. Hsiung, *Mater. Chem. Phys.* **2000** *63*, 19–23.
[4] R. Shapira, C. H. J. Chou, *Biochem. Biophys. Res. Commun.* **1987**, *146*, 1342.
[5] S. Z. Zhang, X. J. Fu, H. Wang, Y. J. Yang, *J. Sep. Sci.* **2008**, *31*, 3782-3787.

Electrochemical Studies on Carbon Based Electrodes Modified with Single and Multi Wall Carbon Nanotubes - Polymer Nanocomposites

Cecilia Cristea[1], Mihaela Tertiş[1], Anca Florea[1], Iuliu Ovidiu Marian[2], Robert Săndulescu[1]

[1]Analytical Chemistry Department, Faculty of Pharmacy, "Iuliu Haţieganu" University of Medicine and Pharmacy, 4 Pasteur Street, 400349, Cluj-Napoca, Romania
[2]Department of Chemistry, Faculty of Chemistry and Chemical Engineering, "Babeş Bolyai" University, 11 Arany Janos St., 400295 Cluj-Napoca, Romania
ccristea@umfcluj.ro

Advances in nanoscience have allowed scientists to incorporate new nanomaterials in biosensing platforms. Carbon nanotubes (CNTs) are one of the allotropic forms of carbon consisting of sp^2 hybridized carbon atoms arranged in graphene sheets, which are rolled up to form tubes. CNTs are nanomaterials that facilitate the charge transfer between the bioelement and the transducer. When CNTs are incorporated into polymeric matrices, properties such as capacitance are greatly enhanced due to the high electroactive surface area which is attributed to the 3D porous nanostructure of the electrode modified with CNTs. Electrochemical impedance spectroscopy was used to characterize the electrodes modified with different types of carbon nanotubes (single and multi-wall) according to their morphology and electrochemical behavior, as shows the previously published results [1]. By using Nyquist and Bode diagrams it was possible to assign the appropriate equivalent circuit, considering all factors that influence the processes occurring at the electrode surface. The main goal was the choice of an improved nanocomposite material for biosensing purposes. The incorporation of single and multi wall CNTs into layer by layer (LBL) films containing enzymes enhances the electron diffusion through the films and the electrochemical surface area, increasing the response of the sensor. In the same time, the enzyme adsorption directly on the CNT reduces the distance between the active site of enzyme and the electrode surface [2, 3]. CNTs provide also a homogeneous porous composite film that facilitates substrate transfer.
The horse radish peroxidase was immobilized onto the glassy carbon electrode surface by entrapment into polymer films of polyethyleneimine doped with SWCNT or MWCNT.
By using Nyquist diagram it was possible to evaluate the R_{ct} in the case of five type of CNT (one SW and four MW) having small morphological differences. A mechanism was proposed to describe the processes that take place at the modified interface. The time constants were also calculated for the two processes occuring at the modified electrodes. The equivalent circuits were proposed and the Kramer-Kronig tests were performed in order to prove their reliability.

Acknowledgements

This paper was published under the frame of European Social Found, Human Resources Development Operational Programme 2007-2013, project no. POSDRU/159/1.5/S/138776. The authors are grateful for the financial support to the Romanian National Authority for Scientific Research, CNCS - UEFISCDI, for the project number PN-II-ID-PCE-2011-3-0355.

References

1. M. Tertiş, A. Florea, B. Feier, I.O. Marian, L. Silaghi-Dumitrescu, A. Cristea, R. Săndulescu, C. Cristea, *J. Nanosci. Nanotechnol.*, 15(5), 3385 **(2015)**
2. J. Q. Liu, M. N. Paddon-Row, J. J. Gooding, *J. Phys. Chem. B* 108, 8460 **(2004)**
3. J. X. Wang, M. X. Li, Z. J. Shi, N. Q. Li, Z. N. Gu, *Anal. Chem.* 74, 1993 **(2002)**

Elucidation of Transport of Environmentally Important Compounds across Model Membranes

Kateřina Nováková [a,b], Tomáš Navrátil [a], Ivana Šestáková [a], Jan Langmaier [a], Romana Sokolová [a],
Jana Jaklová Dytrtová [c], Jaromíra Chýlková [b]

[a] *J. Heyrovský Institute of Physical Chemistry of the AS CR, v.v.i.,*
Dpt. of Biomimetic Electrochemistry, Dolejškova 3, 182 23 Prague 8, Czech Republic
Katerina.Novakova@jh-inst.cas.cz
[b] *University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering, Studentská 573, 532 10 Pardubice, Czech Republic*
[c] *Institute of Organic Chemistry and Biochemistry AS CR, v.v.i., Flemingovo náměstí 2, 166 10 Prague 6, Czech Republic*

Biomembranes represent an interface between outer and inner medium of the cell. Depending on their structure biomembranes have very complex function. Model lipid membranes are used for more detailed information about properties of membrane and about processes associated with biological membrane [1, 2].

Model phospholipid membranes (PLMs) were formed in pores of hydrophilic polycarbonate substrate situated between two Teflon parts in electrochemical cell developed by our research group [3, 4]. We have focused our attention on formation of PLMs from pure phospholipid (1,2-dipalmitoyl-*sn*-glycerol-3-phosphocholine) and from phospholipid with incorporated real parts of biomembranes obtained from protoplasts gained from barley cells by optimized technique. The PLMs and the transporting processes were characterized by electrochemical methods (electrochemical impedance spectroscopy (EIS)) as well as by non-electrochemical methods (optical microscopy, fluorescence microscopy, atomic force microscopy (AFM), electrospray ionization mass spectrometry (ESI-MS).

Cadmium ions and phytochelatins were chosen as representative model species for transport across prepared and characterized PLMs [5, 6]. Incorporation of real parts of biomembranes from protoplasts with natural transporters was confirmed by different amount of transported species detected by voltammetric methods [7, 8].

References

[1] T. Navratil, I. Sestakova, and V. Marecek, International Journal of Electrochemical Science 6 (2011) 6032.
[2] M. Parisova, T. Navratil, I. Sestakova, J. Jaklova Dytrtova, and V. Marecek, International Journal of Electrochemical Science 8 (2013) 27.
[3] T. Navratil, I. Sestakova, and V. Marecek, in Modern Electrochemical Methods XXIX 2009 Eds: J. Barek and T. Navratil), Best Servis Usti nad Labem, Jetrichovice, Czech Republic, pp. 74.
[4] K. Novakova, T. Navratil, I. Sestakova, V. Marecek, and J. Chylkova, in Modern electrochemical Methods XXXIII 2013 Eds: T. Navratil, M. Fojta, and K. Peckova), Best servis Usti nad Labem, Jetrichovice, Czech Republic, pp. 128.
[5] K. Novakova, T. Navratil, I. Sestakova, M. Phuong Le, H. Vodičková, B. Zámečníková, R. Sokolova, J. Bulíčková, and M. Gál, Monatshefte fur Chemie (2015) Accepted; DOI 10.1007/s00706.
[6] J. Dytrtova Jaklova, M. Jakl, K. Novakova, T. Navratil, and V. Šádek, Monatshefte fur Chemie (2015) Accepted; DOI 10.1007/s00706.
[7] B. H. Cruz, J. M. Diaz-Cruz, I. Sestakova, J. Velek, C. Arino, and M. Esteban, Journal of Electroanalytical Chemistry 520 (2002) 111.
[8] I. Sestakova and T. Navratil, Bioinorganic Chemistry and Applications 3 (2005) 43.

Acknowledgements

The research was supported by GA CR (project No. P208/12/1645), by University of Pardubice (SGSFChT for year 2015), and by Academy of Sciences of the Czech Republic (project No. M200401201).

Characterization of Innovative Graphene based Modified Electrodes for Pharmaceutical Analysis

Robert Săndulescu, Oana Hosu, Luminiţa Fritea, Cecilia Cristea, Mihaela Tertiş
Analytical Chemistry Department, Faculty of Pharmacy, "Iuliu Haţieganu" University of Medicine and Pharmacy, 4 Pasteur Street, 400349, Cluj-Napoca, Romania
rsandulescu@umfcluj.ro

Graphene, a two-dimensional carbon-based nanomaterial, attracted great interest in recent years. Their unique properties such as: exceptional thermal and mechanical properties, high specific surface area, excellent electrochemically catalytic activity generated their broad use in electrochemical sensing and bio-sensing [1]. Graphene oxide is a chemically functionalized graphene with groups such as –COOH; -OH or epoxide that is soluble in polar solvents increasing the suspensions stability. The presence of functional groups and metallic impurities in the graphene structure facilitates the biocomponent attachment improving the accuracy of the sensors [2].

Two different procedures were used for graphene oxide functionalization aimed to obtain materials suitable for biosensor development. The first one deals with the chemical reduction of graphene oxide in the presence of β-cyclodextrin and ascorbic acid. During the second protocol the graphene oxide sheets were suspended in a NHS/EDC mixture (100 μM/400 μM) and the succinimide moieties reacted with the graphene oxide carboxylic groups in the presence of EDC forming esters with groups that are easy to remove. This step activates the graphene oxide in order to react with the amine groups from antiacetaminophen antibody (antiAPAP Ab) within amides bonds.

The two types of modified graphene were deposited onto glassy carbon and graphite based screen-printed electrodes via a layer-by-layer method, used for the first time by Haddad *et al.* [3] and also by our team onto single-walled carbon nanotubes [4]. Successive layers of modified graphene oxide were deposited on the electrode surface by adding volumes of graphene suspension, and then dried till complete water evaporation. The obtained nanostructured platform was used for antiAPAP Ab immobilization during the immunosensor development which was successfully applied for acetaminophen detection [5].

The modification protocol used in the case of reduced graphene oxide modified with β-CD was as follows: volumes of graphene suspension were dropped onto the electrode, dried in the oven, and then tyrosinase solution was dropped and dried. Finally a PEI solution was used to immobilize the graphene and enzyme film. This platform was used for the selective and sensitive detection of dopamine in synthetic and real samples.

The structural features of the films deposed onto electrodes were characterized by FTIR, Raman spectroscopy and optical microscopy. EIS experiments were used to characterize the electron transfer properties of the electrode surface during all the modification steps. Cyclic voltammetry determinations were carried out in $[Fe(CN)_6]^{3-/4-}$, $Ru(NH_3)_6Cl_3$ and $Fc(MeOH)_2$ solutions. Cyclic voltammograms were recorded in multisweep conditions and were used for qualitative characterization of the accumulation/rejection phenomena and also the mass transport through the various films.

Acknowledgements

This paper was published under the frame of European Social Found, Human Resources Development Operational Programme 2007-2013, project no. POSDRU/159/1.5/S/136893. The authors are grateful for the financial support to the Romanian National Authority for Scientific Research, CNCS - UEFISCDI, for the project number PN-II-ID-PCE-2011-3-0355.

References

1. S. Kochmann, T. Hirsch, O.S. Wolfbeis, *Trends in Analytical Chemistry* **2012**, *39*, 89-113;
2. M. Pumera, Y. Miyahara, *Nanoscale* **2009**, *1*, 260–265;
3. R. Haddad, S. Cosnier, A. Maaref, M. Holzinger, *Analyst* **2009**, *134*, 2412-2418;
4. M. Tertiş, A. Florea, R. Săndulescu, C. Cristea, *Sensors* **2013**, *13*, 4841-4854.
5. M. Tertiş, O. Hosu, L. Fritea, C. Farcău, A. Cernat, R. Săndulescu, C. Cristea, *Electroanalysis* **2015**, *accepted*.

The Analysis of Solid Electrolyte Interphase on Graphitic anode

Yong Liu*, Kai Xie, Chunman Zheng, Yi Pan, Yujie Li, Hui Wang
College of aerospace science and engineering, National university of defense technology.
Changsha, Hunan, China
E-mail:liuzi244@qq.com

The Solid electrolyte interphase (SEI) formed on the graphite anode was thought to be the key factors effecting the rate performance, cycle life and calendar life of commercial lithium batteries[1]. To get a better understanding of SEI, the surface chemistry components of anode and its depth profile study was carried out by X-ray photoelectron spectroscopy[2]. Before the XPS study, the anode cycled 3 times at a rate of C/3 at room temperature, then storaged for 1 day at 40℃ and cycled another 3 times through assembling bag cell using $LiCoO_2$ as cathode so that fully formed SEI could be generated. The XPS spectra showed that the surface of anode was fully coated with semicarbonate species and some inorganic species, however, after continuous Ar^+ sputtering on the anode, it was found that when sputtering longer, the amount of semicarbonate species decreased, but the amount of inorganic species LiF increased after sputtering 15s and then decreased when sputtering time getting longer.

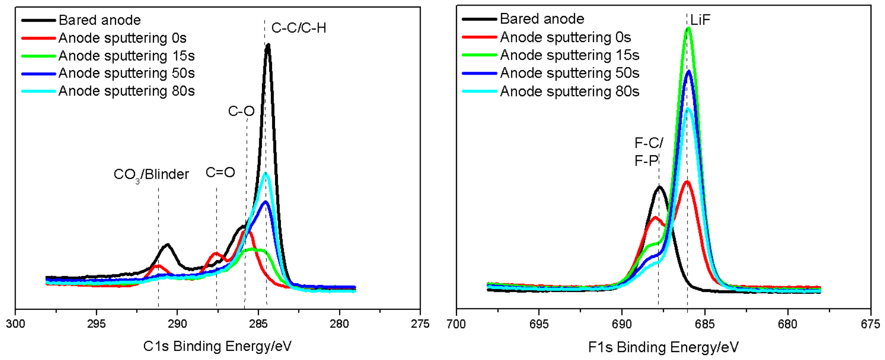


Fig.1 XPS C1s and F1s spectra of anode

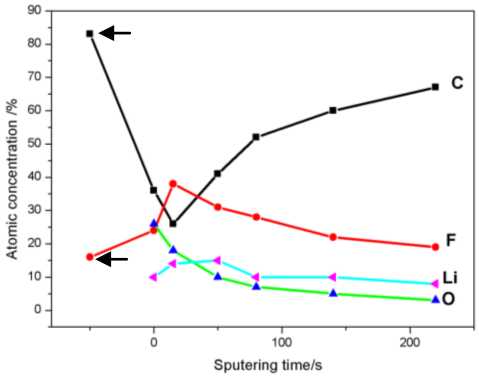


Fig.2 The changes of atomic concentration upon sputtering time (the arrowed point was the atomic concentration of bared anode)

References:
[1] Pallavi Verma, Pascal Maire, Petr Novak. A Review of The Features and Analyses of The Solid Electrolyte Interphase In Li-ion Batteries. Electrochimica Acta. 2010, 55: 6332-6341.
[2] Katarzyna Ciosek Hogstom, Sara Malmgren, Maria Hahlin, et al. The Buried Carbon/Solid Electrolyte Interphase in Li-ion Batteries Studied by Hard X-ray Photoelectron Spectroscopy. Electrochimica Acta. 2014, 138: 430-436.

Onset potential determination at gas-evolving catalysts by means of constant-distance mode positioning of nanoelectrodes

Alexander J. R. Botz[a], Michaela Nebel[b], Edgar Ventosa[a], Wolfgang Schuhmann[a]
[a]*Analytical Chemistry - Center for Electrochemical Sciences (CES);*
Ruhr-Universität Bochum, Universitätsstr. 150; 44780 Bochum; Germany
[b]*Sensolytics GmbH, Universitätsstr. 142, 44799 Bochum, Germany*
Alexander.Botz@rub.de

Beside other attributes the onset potential is an important indicator for the activity of electrocatalysts. Especially in the case of gas evolving catalysts it is a challenge to separate the gas evolving reaction from e.g. other faradaic side reactions at the catalyst material, which may occur in a similar potential region as the onset potential of the gas evolution reaction.

The black current-potential curve (Fig. 1) measured at a sample of RuO_2 demonstrates such a superposition of the analytical signal by different effects. A side reaction, probably the oxidation of ruthenium, overlays the region of the expected onset potential. As a result, the onset potential determined by classical method is shifted to a more anodic potential.

In order to circumvent these inaccuracies and to minimize further external factors, caused i.e. by the addition of binders, a sub-micrometer sized electrode was positioned closely to the catalyst immobilized in a microcavity electrode using shearforce-based constant-distance mode scanning electrochemical microscopy (SECM). Potential control at the tip guarantees a species selective data acquisition. Furthermore, the small size of the SECM probe leads to an improved signal-to-noise ratio (as depicted in Fig. 1 grey curve) and consequently a highly sensitive oxygen determination. This allows an accurate determination of the onset potential at a catalyst modified microcavity electrode and provides a general strategy for the investigation of gas evolving catalysts.

To directly prove the validity of the experiment and to compare the onset potential with an internal reference, a three point method, utilizing a double-barrel microcavity electrode, was applied. By comparing different oxygen evolution catalysts with the benchmark RuO_2 in one experiment, a precise determination of the onset potential of the catalyzed reaction became feasible.

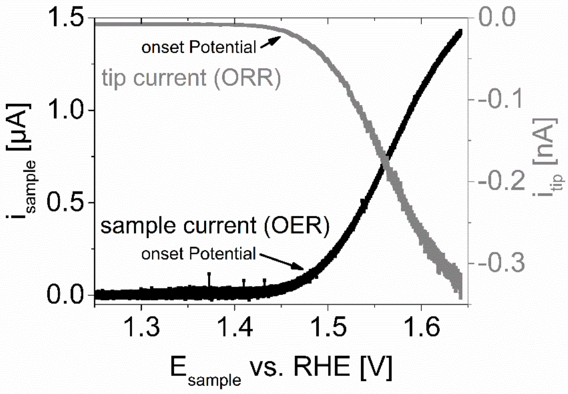


Fig. 1: Current-potential curves at a microcavity electrode (100 µm Ø) filled with RuO_2. The sample current (black) and SECM tip current (grey) are plotted versus the potential applied at the microcavity electrode. (SECM tip: Pt disk electrode with 0.8 µm Ø, 0.1 M NaOH; v = 1 mV/s).

Acknowledgement: The supply of the perovskites by Dr. Frank Tietz (Forschungszentrum Jülich GmbH; IEK-1; Wilhelm-Johnen-Straße, 52425 Jülich; Germany) and the Financial support from the Helmholtz-Energie-Allianz "Stationäre elektrochemische Speicher und Wandler" (HA-E-0002) is gratefully acknowledged.

Coupled FTIR-GC/MS for *in-situ* characterization of gas species emitted from Lithium Ion Batteries

Irina Gocheva[1*], Alfred Amon[1], Wolfgang Märzinger[2], Erwin Rosenberg[3], Roman Binder[4], Atanaska Trifonova[1]
[1]*AIT Austrian Institute of Technology, Mobility Department, Electric Drive Technology, Giefinggasse 2, 1020 Vienna, Austria*
[2]*i-RED Infrarot Systeme GmbH, Hafenstrasse 47-51, 4020 Linz, Austria*
[3]*Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9, 1060 Vienna, Austria*
[4] *Shimadzu, Laaer Strasse 7-9, 2100 Korneuburg, Austria*
irina.gocheva@ait.ac.at

With implementation of large battery packs in vehicular systems the development of hyphenated methods for battery safety examination becomes important. Coupling of high- resolution separation techniques such as GC/MS (& LC/MS) capable to detect traces with FTIR where the resulting spectrum of absorbed irradiation works as a molecular fingerprint of the sample makes possible to collect information about unknown materials, gas species evolved during the battery performance under normal and/or abuse conditions, regressive recognition of battery components, and determination of the amount of components in a mixture. Indeed GC/MS has been used for postmortem analysis of battery fails [1, 2] however the technique lacks temporal resolution for *in-situ* classification. A major obstacle for the development of new high voltage batteries and improved battery safety comes from the poor stability of the prevailing liquid organic electrolytes used. The consequences of battery failure and overcharge are well known nevertheless for better understanding of the complex rapid processes inside the batteries a suitable technique is desirable. Herein we present a recently developed *in-situ* method for estimation of gas species evolved from different battery and electrolyte systems which combines unique identification and quantification with excellent time resolution. The decomposition behavior for commercially used electrolytes under different charge/discharge conditions with consideration to the influence of the electrode material on the onset potential of electrolyte oxidation and reduction reactions were examined.

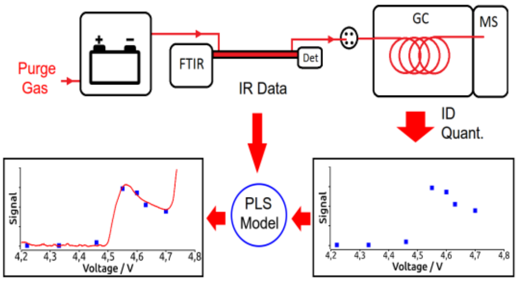


Fig. 1: Scheme of the measurement and data modelling process

This work was funded by the Austrian Research Promotion Agency (FFG, Project Number 835790).

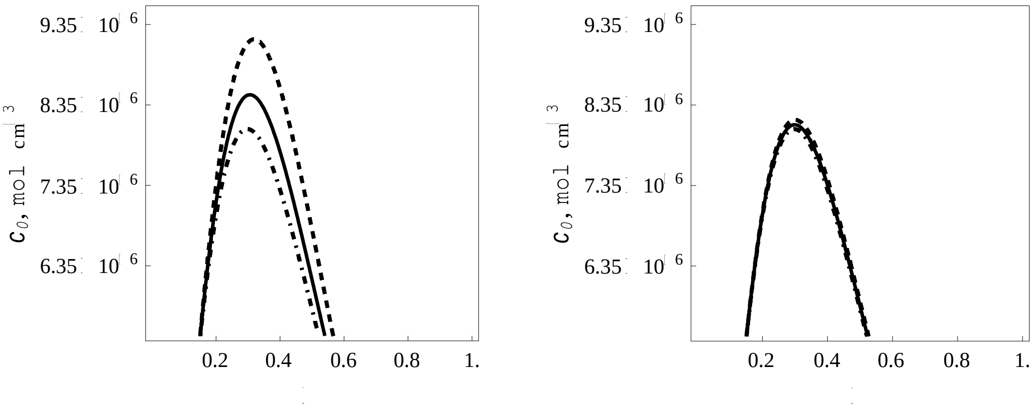
[1] G. Gachot et al., Gas chromatography/mass spectrometry as a suitable tool for the Li-ion battery electrolyte degradation mechanisms study, Anal. Chem. 83 (2011) 478.
[2] M. Holzapfel, A. Würsig, W. Scheifele, J. Vetter, P. Novák, Oxygen, hydrogen, ethylene and CO_2 development in lithium-ion batteries, J. Power Sources 174 (2007) 1156.

Dynamic Instabilities at Electrified Interfaces of Different Geometry

Gichan O.I., Pototskaya V.V.
Chuiko Institute of Surface Chemistry, Ukrainian National Academy of Sciences
17, Henerala Naumova Str., 03164 Kyiv, Ukraine
Vernadskii Institute of General & Inorganic Chemistry, Ukrainian National Academy of Sciences
32-34, Palladina Prosp., 03142 Kyiv, Ukraine
gichan@meta.ua, pototskaya@ionc.kiev.ua

We investigate oscillatory and bistable dynamics in a model electrocatalytic process with a preceding chemical reaction in the Nernst diffusion layer and the potential-dependent adsorption/desorption of electroactive species at spherical, cylindrical and planar electrodes under potentiostatic conditions.

In terms of the Gerischer impedance the conditions for the Hopf and saddle-node instabilities were calculated. The potential range where the Hopf instability leading to periodic current oscillations can be realized is the largest in case of a planar electrode and it is the smallest for a spherical electrode. The situation in case of saddle-node instability giving rise to multistability of steady state is opposite. Fig. 1 shows a variation of the bistability region limited by the curve of the polarization resistance zeros depending on electrode size and its form.



(a) (b)

Fig. 1. Bistability region in plane of bulk concentration of electroactive species c_0 and electrode surface coverage by adsorbate θ for spherical (dashed line), cylindrical (solid line) and planar (dot-dashed line) electrodes at two values of spherical and cylindrical electrode radius r_0: (a) $r_0 = 10^{-4}$ cm; (b) $r_0 = 10^{-3}$ cm.

Electronic Tongue for Simultaneous Determination of Cyanide, Thiocyanate and Iodide

Abbas Shirmardi[a*], Mojtaba Shamsipur[b], Morteza Akhond[c]

[a] *Department of Chemistry of Masjed-Soleiman Branch, Islamic Azad University, Masjed-Soleiman, Iran*
[b] *Department of Chemistry, Razi University, Kermanshah, Iran*
[c] *Department of Chemistry, Shiraz University, Shiraz, Iran*

[*]Corresponding author: Tel.: +986813331181; Fax: +986813336319.
Email address: ashirmardi.abbas@gmail.com (Abbas Shirmardi)

Abstract

Five cross selective electrodes comprising cyanide, thiocyanate, and iodide coated graphite electrodes CGEs were used as sensing parts an electronic tongue for simultaneous determination of cyanide, thiocyanate, and iodide ions in the presence and the absence of chloride ion as a coexisting ion. The CGEs were constructed using poly vinyl chloride chloride (PVC), o-nitrophenylocthyl ether (o-NPOE), cethyl tetrabuthylamonium bromide (CTAB), and metalphorphyrin complexes as ionophores. The constructed electrodes were characterized to obtain their calibration curve, response time, and repeatability.

A programmed switching system combined with an array of the five potentiometric coated graphite electrodes (i.e., ion-selective or cross-selective electrodes) were connected directly to a pH/potentiometer and a computer to sequentially acquire the potential corresponding to water sample mixtures. The acquired potentials were recorded and saved on the computer and were used as input variables for an artificial neural network to simultaneously yield the concentrations of cyanide, thiocyanate and iodide ions in simple and complex mixtures. A feed-forward, back propagation network with a Levenburg–Maquart algorithm was employed to optimize the network parameters.

Key words: Electronic Tongue; Cyanide; Thiocyanate; Iodide; Artificial Neural Network

---

A new approach towards understanding of the ion transfer dynamics in nanostructured carbon films for energy storage applications

F. Escobar Teran[a,b], C. Gabrielli[a,b], H. Perrot[a,b] and O. Sel[a,b]

[a] *Sorbonne Universités, UPMC Univ. Paris 06, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques, F-75005, Paris, France*
[b] *CNRS, UMR 8235, LISE, F-75005, Paris, France*

The efficiency of energy storage devices depends largely on the physical properties of the materials that are constituted of, such as the specific surface area, porosity and/or morphology [1,2]. It is therefore necessary to characterize and to control the parameters that play a predominant role for the performance of these materials. Particularly, the morphology dependent performance, and kinetic or dynamic aspects of ion electroadsorption behaviour of carbon based electrodes is not a quite solved issue. In the literature, the interaction of ions with carbon based electrodes was investigated by *in situ* and *ex situ* characterization techniques, including electrochemical and gravimetric methods. However, none of these methods alone provides the information on the exact identification of the electroadsorbed ionic species, their dynamics of transfer at the interfaces, as well as the role of electrolyte composition and the effect of ions solvation on the charge storage phenomena. Therefore, in this work, an alternative characterization tool was proposed which couples fast quartz crystal microbalance (QCM) and electrochemical impedance spectroscopy (EIS) (*ac*-electrogravimetry). Films of carbon nanotubes (SWCNT) were chosen as nanostructured electrodes materials and tested in aqueous electrolytes containing different ions such as Li^+, Na^+ and K^+. The chemical nature and the role of each species, anion, cation, solvated ions, free solvent, directly or indirectly involved in the charge storage, have been identified *via* the measures of *ac*-electrogravimetry. Specifically, experimental results showed that hydrated cations and protons ($Li^+.H_2O$, H^+ and $Na^+.H_2O$, H^+, in aqueous LiCl and NaCl, respectively) were electroadsorbed when the carbon nanotube surface was negatively charged, and the contribution of the anionic species was identified when the surface was positively charged. More importantly, we could access to the kinetic information on the transfer of these species on the carbon nanotube surface by changing the frequency of the potential modulation which permits to separate faster and slower process. The transfer of hydrated lithium, and hydrated sodium occurs at high frequencies (faster) and that of the proton occurs at lower frequencies (slower). Accordingly, the transfer resistance of hydrated lithium, and hydrated sodium and free solvent is lower than that of the transfer of H^+, indicating the ease of larger ions transfer. The contribution of free solvent molecules were also identified which occurred at high frequencies. Interestingly, despite the slow kinetics and high transfer resistance values, the contribution of protons in the charge storage is not negligible. These results may be correlated to several phenomena including (i) the differences in the dehydration kinetics of $Li^+.nH_2O$ (in the bulk of the solution) to $Li^+.H_2O$ and to that of ($H^+.nH_2O$) to H^+, and (ii) the different sites (different pore dimension) of electroadsorption in the porous carbon nanotube based electrode. Additionally, the relative concentration changes of the species were determined which permitted us to construct the mass variations of the electrode as a function of the applied voltage. These independent measurements exhibited perfect agreement with the classical electrochemical quartz crystal microbalance (EQCM) measurement results. These findings strongly suggest that *ac*-electrogravimetry is an appropriate tool to characterize complex charge storage behavior of carbon electrodes. It deconvolutes the global gravimetric response of EQCM and provides additional information such as the exact identification and the respective mass variations of species, and as well as the kinetic information of their electroadsorption/electrodesorption. To the best of our knowledge, an unambiguous identification of electroadsorbed species, the information on their transfer dynamics and quantification of the transferred species have never been reported in the literature.

References :

[1] P. Simon, Y. Gogotsi, *Nature Mater.* 2008, **7,** 845.
[2] J. R. Miller, P. Simon, *Science* 2008, **321** 651.
[3] W. Tsai, P. Taberna, P. Simon, *J. Am. Chem. Soc.*, 2014, **136**, 8722.

Polypyrrole Nanotubes with Noble-Metal Nanoparticles and their Carbonized Analogues

I. Sapurina[1,2], J. Stejskal[1], M. Trchová[1]
[1] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,*
162 06 Prague 6, Czech Republic
[2] *Institute of Macromolecular Compounds, Russian Academy of Sciences,*
St. Petersburg 199004, Russian Federation
stejskal@imc.cas.cz

Polypyrrole nanotubes were prepared by the oxidation of pyrrole with iron(III) chloride in the presence of methyl orange [1]. They were subsequently used as a substrate for the reductive deposition of noble-metal particles. Polypyrrole nanotubes decorated with palladium, platinum, rhodium, or ruthenium nanoparticles (Figure) were characterized by electron microscopy, conductivity, energy dispersive X-ray analysis, and FTIR and Raman spectroscopies. A typical metal content varied between 15–20 wt.%. The carbonization of resulting composites has been followed during thermogravimetric analysis in nitrogen atmosphere up to 800 °C. The nanotubular morphology of polypyrrole was retained after carbonization. The noble-metal nanoparticles, however, fused to clusters during this process except for ruthenium.

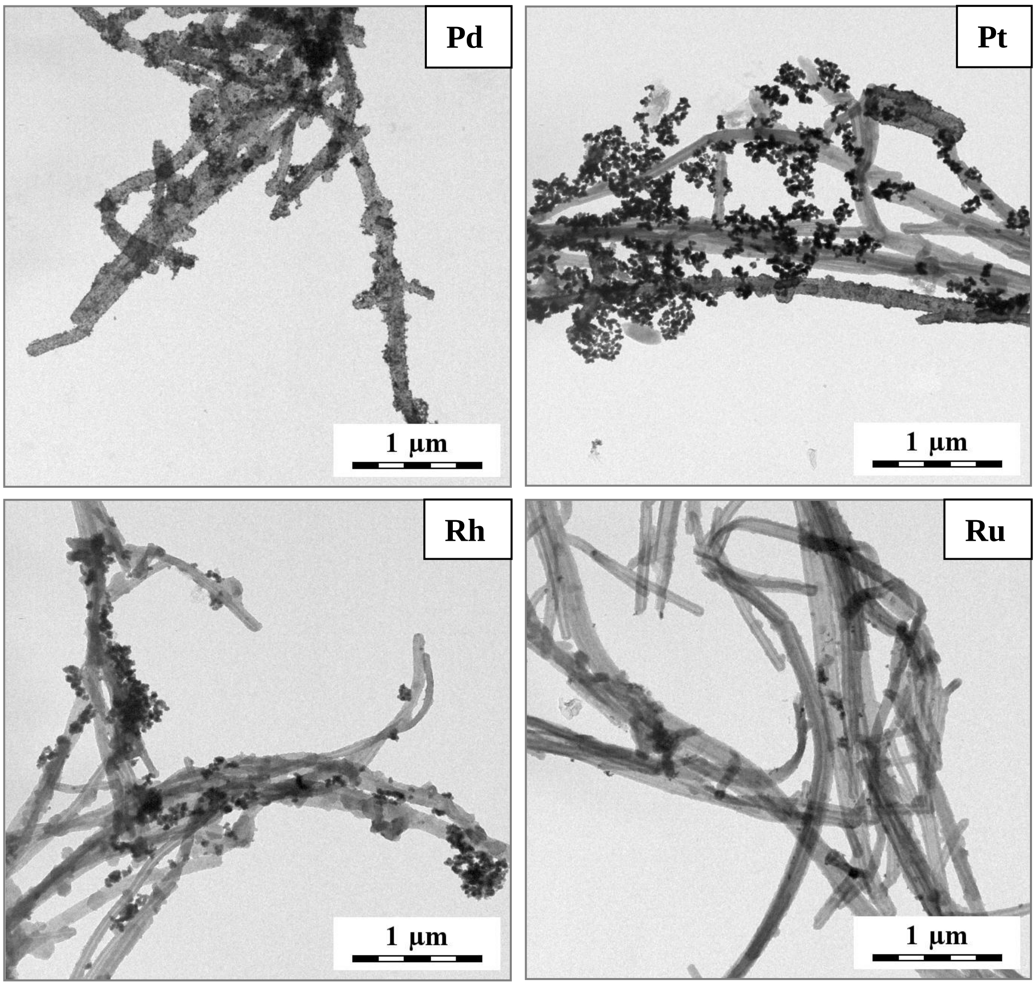


Figure. Polypyrrole nanotubes decorated with palladium, platinum, rhodium, and ruthenium nanoparticles.

[1] Kopecká J., Kopecký D., Vrňata M., Fitl P., Stejskal J., Trchová M., Bober P., Morávková Z., Prokeš J., Sapurina I., RSC Advances 4, 1551–1558 (2014).

Conducting Materials Prepared by the Oxidation of *p*-Phenylenediamine with *p*-Benzoquinone

M. Trchová, J. Stejskal, Z. Morávková, M. Bláha
Instiute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
162 06 Prague 6, Czech Republic
trchova@imc.cas.cz

Poly(*p*-phenylenediamine) is typically prepared by the oxidation of the corresponding monomer with ammonium peroxydisulfate [1,2]. The replacement of peroxydisulfate with an organic oxidant, *p*-benzoquinone, however, leads to the oligomer incorporating *p*-benzoquinone constitutional units along with *p*-phenylenediamine ones (Figure), in the accordance with similar the experiments on aniline oxidation with *p*-benzoquinone [3]. Such products are conducting and may be suitable as new materials in solid-state electrochemistry.

In the first series of experiments, *p*-phenylenediamine (0.2 M, Sigma Aldrich) was oxidized with *p*-benzoquinone (0.5 M, Sigma Aldrich) in aqueous solutions of methanesulfonic acid (MSA) of various concentrations. In another series of experiments, the mole ratios of *p*-benzoquinone to *p*-phenylenediamine were varied from 0.5 to 2.5 at fixed 1 M concentration of MSA.

The conductivity of the products increased with increasing concentration of MSA from 1.5×10^{-12} S cm^{-1} in 0.1 M MSA up to 3.4×10^{-4} S cm^{-1} in 5 M MSA. The low-molecular-weight products are basically composed of one *p*-benzoquinone and two *p*-phenylenediamine molecules, and they are able to produced salts with acids (Figure). The molecular structure of the reaction products is discussed on the basis of mass, FTIR, and Raman spectroscopies.

The electrical properties enabling the potential applications in organic electronics, however, have not yet been addressed and are reported in the present communication. Electrorheology is another field where materials of this type are applicable [4].

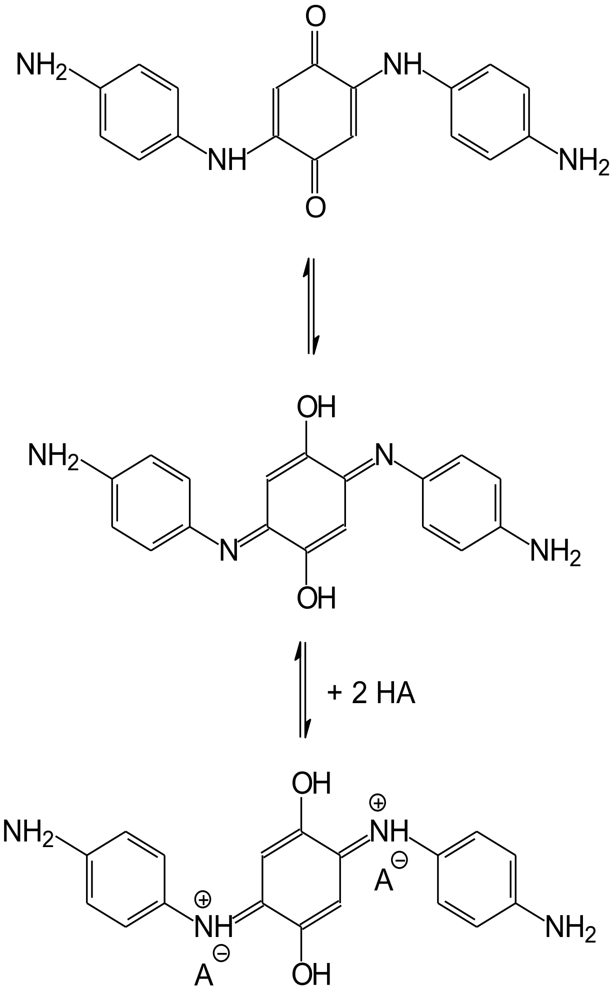


Figure. After "keto–enol" rearrangement, imine nitrogen atoms are protonated with an acid (HA) to produce a corresponding salt.

References

1. Stejskal J, Trchová M. Polym. Int. 61 (2012) 240–251.
2. Stejskal J. Prog. Polym. Sci. (2014), in press; doi: 10.1016/j.progpolymsci.2014.10.007.
2. Stejskal J, Bober P, Trchová M, Horský J, Pilař J, Walterová Z. Synth. Met. 192 (2014) 66–73.
3. Plachy T, Sedlacik M, Pavlinek V, Morávková Z, Hajná M, Stejskal J. Carbon 63 (2013) 187–195.

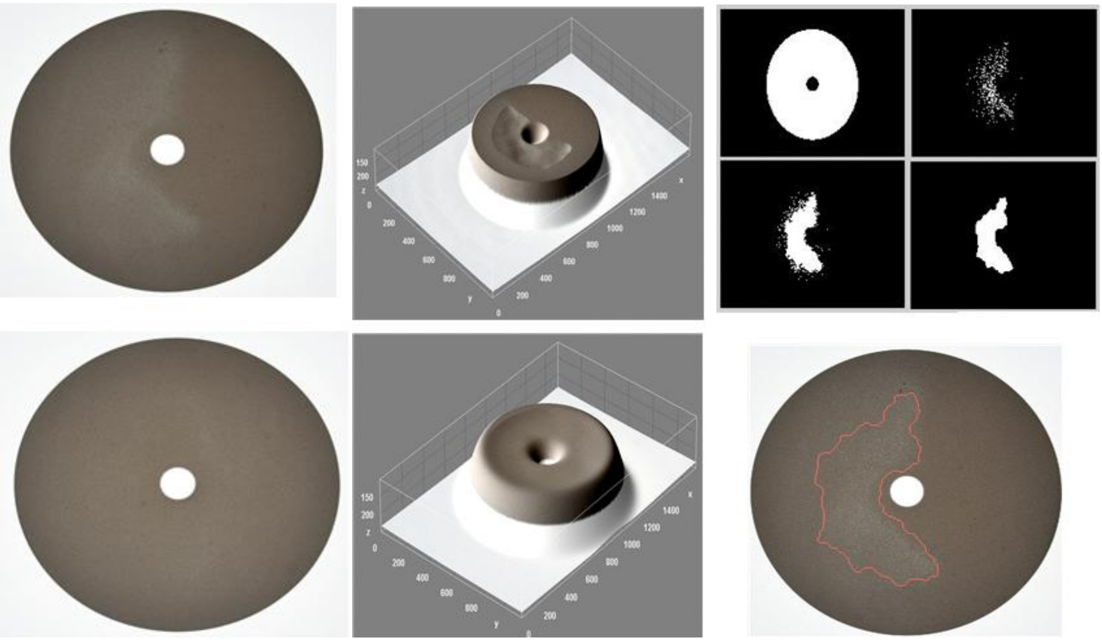
A multi-scale image analysis for the electrolyte and stacking sequence of thermal activated batteries

Sang-hyeon Ha, Sung-baek Cho
Agency for Defense Development
Yuseoung P.O. Box 35-41, Daejeon 305-600, Korea
shha@add.re.kr

For the development of reliable thermal activated batteries, an electrolyte is quite important because it is closely related to the discharge performance and stability of thermal batteries. The cracks and low-density of an electrolyte can give rise to bridging electrodes and cause discharge failure and inner short of electrodes. And a stacking sequence of electrodes and electrolytes is also important because thermal battery is a kind of layer-built cells. If there is some problems of stack sequences (ex, out of order), thermal batteries will be unstable and burst out.

This paper includes two parts of multi-scale image analysis. At first, this paper describes multi-scale image processing methods used for analysis of molten-salt based electrolyte disk and also describes how we can apply this image processing method to the analysis of thermal battery electrolyte. Moreover, we have found optimized image processing conditions to improve the discriminating ability of compaction defects such as non-uniform parts in an electrolyte. This multi-scale analysis was carried out using the IMAGE J program.

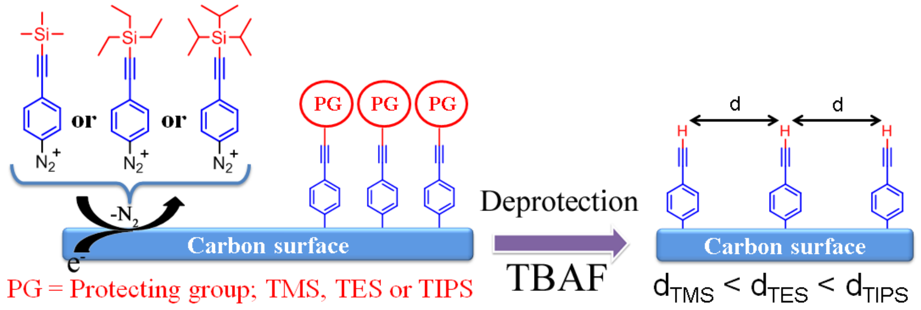
Secondly, this paper describes multi-scale image processing methods of stacking sequence of electrodes and electrolytes. Especially, we focused on grouping and classification the order of electrodes and electrolytes using edge detection methods. This multi-scale analysis was carried out using the Image Toolkit of Labview program.



Nanostructured Monolayers on Carbon Substrates.

Yann R. Leroux, Philippe Hapiot
Institut des Sciences Chimiques de Rennes, CNRS, Université de Rennes 1
263, avenue du Général Leclerc, Campus de Beaulieu, Bat 10C, Rennes, 35042 France
yann.leroux@univ-rennes1.fr

The electro-generation of aryl radicals from protected aryl diazonium salts combined with protection-deprotection steps[1] was evaluated to design functional monolayers on carbon substrates with a well-controlled organization of the modifier at the molecular scale. The influence of the size of different silyl protecting groups on resulting covalently bounded films were investigated. Three different protecting groups were considered: trimethylsilyl (TMS), triethylsilyl (TES) and tri(isopropyl)silyl (TIPS). When the active function was introduced on para position of the aryl ring, a robust ethynylaryl monolayer is obtained after deprotection whatever the substituent. Electrochemical and structural analyses show that the organization of the attached monolayer is totally governed by the size of the protecting group. Properties of the monolayer (charge transfer, permeation of molecules through the layer, density of functional groups) were examined in combination of the performances for post-functionalization taken an alkyl-ferrocene derivative as an example of immobilized species. As a remarkable feature, all layers present large density of active alcyne terminations that remain totally available for further "click chemistry" coupling.[2]



References:
(1) Y. R. Leroux, H. Fei, J.-M. Noël, C. Roux, P. Hapiot, Efficient Covalent Modification of a Carbon Surface: Use of a Silyl Protecting Group To Form an Active Monolayer J. Am. Chem. Soc. 132 (2010) 14039.
(2) Y. R. Leroux, P. Hapiot, Nanostructured Monolayers on Carbon Substrates Prepared by Electrografting of Protected Aryldiazonium Salts. Chem. Mater. 25(3) (2013) 489.

Two Related Electrochemical Active Phosphites: $Li_{1.43}[Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO_3)_6]\cdot1.5H_2O$ (1) and $Li_{0.86}[Fe^{II}_{3.86}Fe^{III}_{1.14}(HPO_3)_6]\cdot0.8H_2O$ (2)

Teresa Berrocal[1], José L. Mesa[1], Edurne S. Larrea[2], Iratxe de Meatza[3], J.-Alberto Blázquez[3], Miguel Bengoechea[3], Jesús Rodríguez-Fernández[4], Andrés T. Aguayo[5], and María I. Arriortua.[2]
[1]Departamento de Química Inorgánica and [2]Departamento de Mineralogía-Petrología, Facultad de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, Apdo. 644, E-48080 Bilbao, Spain.
[3]Departamento de Energía, IK4-CIDETEC, Paseo Miramón 196, Parque Tecnológico de San Sebastián, 20009 San Sebastián, Spain.[4] Departamento CITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain, [5]Departamento de Ingeniería Química, Facultad de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, Apdo. 644, E-48080 Bilbao, Spain.
joseluis.mesa@ehu.es

Research in the area of framework solids exhibiting open structures continues to be exciting because of their many potential applications.[1] $Li_{1.43}[Fe^{II}_{4.43}Fe^{III}_{0.57}(HPO_3)_6]\cdot1.5H_2O$[2] (**1**) and $Li_{0.86}[Fe^{II}_{3.86}Fe^{III}_{1.14}(HPO_3)_6]\cdot0.8H_2O$ (**2**) has been hydrothermally synthesized. In case of **2,** a later dehydration process at 260 ºC has been accomplished. Both phases exhibit a crystal structure formed by a $[Fe^{II}_{3.86}Fe^{III}_{1.14}(HPO_3)_6]^{0.86-}$ porous inorganic framework with the Li^+ cations as counterions. The anionic inorganic skeleton is based on layers of FeO_6 octahedra linked along the *c*-axis through $(HPO_3)^{2-}$ oxoanions. The sheets are constructed by twelve membered rings of FeO_6 octahedra repeated along the *ab* plane giving rise to channels of *ca.* 3 Å diameter along the [100] direction in which the water molecules and Li^+ cations are located, showing positional disorder. The limit of the thermal stability of both materials is approximately 285 °C. The IR spectra show the P-H vibrational bands belonging to the phosphite groups. From the fit of the Mössbauer spectrum, in the paramagnetic state, characteristic values of the isomer shift and quadrupolar splitting for the simultaneous presence of Fe(II) and (III) cations have been obtained. From the AC magnetic measurements, a spin glass behavior was inferred that can be attributed to the presence of both Fe^{II} (S= 2) and Fe^{III} (S= 5/2) cations, in both phases. The spin glass like state was confirmed by specific-heat experiments, being **2** the second ordered transition metal phosphite exhibiting this magnetic behavior. The existence of mobile lithium cation in the channels of both **1** and **2** has been studied by impedance spectroscopy at different temperatures. Electrochemical characterization was completed by cyclic voltammetry experiments and galvanostatic measurements. A reversible exchange of lithium is also observed for the compounds for more than 50 galvanostatic cycles, equivalent to approximately 12 and 10 $mAh.g^{-1}$ of sample, for **1** y **2**, respectively.

Acknowledgements: We gratefully acknowledge financial support of the Gobierno Vasco (IT-630-13, S-PC11UN001, and S-PC12UN007) and the Ministerio de Economía y Competitividad (MAT2013-42092-R). The authors also thank the technicians of SGIker, UPV/EHU, Drs, J. Sangüesa, Dra. Leire San Felices, and Dr. A. Larrañaga for the X-ray diffraction measurements, and Dr. Estibaliz Legarra for the Mössbauer spectroscopy measurements. E. S. Larrea thanks the Gobierno Vasco for her post-doctoral contract (IT-630-13).

---

[1] J. Adams and D. Pendlebury, *Materials Science & Technology,* Thomson Reuters, **2011**.

[2] U-C. Chung, J. L. Mesa, J. L. Pizarro, I. de Meatza, M. Bengoechea, J. Rodríguez Fernández, M. I. Arriortua, T. Rojo, *Chem. Mater.* **2011**, 23, 4317-4330.

Synthesis and Electrochemical Characteristic of Si/C Composite Anode with CNF for Lithium Ion Battery

Jong Dae Lee, Ji Yong Park
Department of Chemical Engineering, Chungbuk National University
52 Naesudong-ro, Heungdeok-gu, Cheongju, Chungbuk, 361-763 Korea
jdlee@chungbuk.ac.kr

In recent years, lithium ion battery, which has a high current density and a high specific energy, has been mainly used as power sources of portable electronic devices and electric/hybrid vehicles. As an anode material for the lithium ion battery, Silicon(Si) is getting attention for its high theoretical specific capacity (about 4200mAh/g) and its proper potential range for lithium insertion and extraction. Nevertheless, the intrinsic limitations of silicon-based anode are the large volume change during lithium alloying-de alloying process and the low electrical conductivity. Recent studies have shown methods such as synthesizing Si into nanospheres, synthesizing mesoporous Si/C composite, or synthesizing ordered porous Si/C to improve the cyclic stability of Si anode. In this study, we synthesize Silicon/Carbon/CNF composites as an anode material to overcome the limitations of the silicon-based anode mentioned above and to enhance the electric conductivity. Si/C/CNF composites were prepared by the fabrication processes including the synthesis of SBA-15, magnesiothermic reduction on the SBA-15 by ball milling to obtain Si/MgO, carbonization of phenolic resin with CNF, and the HCl etching. The prepared Si/C/CNF composites were analysed by BET, XRD, FE-SEM and TGA. Among the SBA-15 samples synthesized with reaction temperatures between 50℃ and 70℃, the SBA-15 of 60℃ showed the largest specific surface area. Also the electrochemical performances of Si/C/CNF composites as the anode electrode were investigated by constant current charge/discharge test, cyclic voltammetry and leakage tests in the electrolyte of $LiPF_6$ dissolved in organic solvents(EC:DMC:EMC=1 :1 :1 vol%). The coin cell using Si/C/CNF composite(Si:CNF=97 :3 in weight) has better capacity(1,387 mAh/g) than that of other composition coin cells. Also, it is found that Si/C/CNF composite(Si:CNF=97:3 in weight) electrode shows improved cycling performance and electric conductivity.

Synthesis, mechanical characterization, electrochemical and corrosion behaviour of titanium-based alloy with “super” properties

S. I, Drob[a], C. Vasilescu[a], D. M. Gordin[b], T. Gloriant[b]
[a]*Institute of Physical Chemistry, 202 Spl. Independentei, 060021, Bucharest, Romania*
[b]*Institut des Sciences Chimiques de Rennes, 20 Avenue de Buttes de Coesimes, F-35043 Rennes Cedex, France*

Titanium-based alloy (Ti–23Nb–0.7Ta–2Zr–1.2O) was synthesized by melting under high vacuum in cold crucible semi-levitation furnace. X-ray diffraction (XRD) profile highlights ß-phase microstructure. The electron backscattered diffraction (EBSD) revealed equiaxed microstructure constituted by body-centered cubic ß phase. The tensile test displays typical mechanical characteristics of the “super alloy”: a very high strength of 900 MP (2.5 times higher than that of CPTi); the Young's modulus has around 60 GPa, very close to that of bone (30 GPa); huge tensile recoverable elasticity is 1.5% (six times higher than of CPTi).

The electrochemical and corrosion behavior of the alloy in comparison with that of CPTi was determined from cyclic potentiodynamic polarization curves, linear polarization measurements (Tafel representation) and monitoring of the open circuit potentials and corresponding open circuit potential gradients in Ringer solutions of different pH values (acid, neutral and alkaline) simulating the human biofluid. The cyclic potentiodynamic polarization curves exhibited self-passivation of the alloy with a very large passive potential range, more electropositive corrosion potentials, more active passivation potentials than those of CPTi that demonstrate a nobler passive behaviour and a more stable passive state. Tendency to passivation is lower for alloy, proving an easier passivation due to the favorable influence of Nb, Ta, Zr alloying elements, which participate with their protective oxides Nb_2O_3, Ta_2O_5, and ZrO_2 to the formation of the alloy passive film.

Corrosion current densities are lower of about 20 times in neutral and of about 3 times in acid and alkaline Ringer solutions for alloy in comparison with those of CPTi. These facts show superior resistance class for alloy and very low quantities of ions released into physiological solutions, namely negligible toxicity of this alloy. Polarization resistances have higher values for alloy, which attest more protective passive film.

The long-term studies by the monitoring of the open circuit potentials evinced nobler values for alloy than those for CPTi, due to its more resistant passive film as was shown from cyclic polarization curves; these values became more electropositive in time and reached about constant values after 500 immersion h, fact that indicates the growth, thickening of the passive film. Open circuit potential gradients have very low values, which can not initiate galvanic cells.

From above presentation it results that the studied alloy presents nobler electrochemical behavior, superior anticorrosive resistance and negligible toxicity in comparison with CPTi, being a suitable material for implantation.

Differences in Li-storage Mechanism into Anatase and TiO_2(B)

M. Zukalova, B. Laskova and L. Kavan
J. Heyrovsky Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic,
CZ-18223 Prague 8, Czech Republic
marketa.zukalova@jh-inst.cas.cz

Amongst various transition-metal oxides, titanium oxides are very attractive Li-ion battery negative electrode materials because they are inexpensive, non-toxic, and reversibly insert Li at a redox potential of around 1.5 V vs. Li^+ /Li. Therefore, various polymorphs of titania such as rutile, anatase and TiO_2(B) have been studied as electrode materials for advanced Li-ion batteries, exhibiting improved lithium-storage properties[1-6]. Generally, Li insertion into rutile and anatase proceeds as a diffusion controlled irreversible process. Due to the low chemical diffusivity of Li in TiO_2, which is rate-determining for the lithium incorporation and extraction reaction, an introduction of a high porosity and surface area by nanosizing of the TiO_2 materials is a key to improved Li^+ diffusion. Because of the increased impact of both the surface and the interface in nanosized materials, so-called interfacial (surface) Li storage can play an important role in nano structured materials beyond the conventional bulk insertion of Li into a titanium dioxide and ternary oxide lattice. Excess Li can be accommodated either at the interfaces of the nanometer-sized particles or at the open channels in the structure of particular polymorphs (TiO_2(B)) by means of a pseudocapacitive faradaic process, which is not controlled by diffusion. In this case, the currents in the peak maxima in cyclic voltammograms of Li insertion scale with the first power of scan rate, which is characteristic for capacitive charging.

Unusually large faradaic pseudocapacitance specific for Li-insertion into TiO_2(B) was ascribed to Li-accommodation in open channels of TiO_2(B) structure allowing fast Li-transport in TiO_2(B) lattice along the b axis (perpendicular to (010) face)[7]. Detailed analysis of cyclic voltammograms of Li insertion into TiO_2(B) and anatase provides information about capacitive contributions to overall charge of Li-storage[8]. The enhancement of 30% is found in capacitive contributions (normalized to the total stored charges) in TiO_2(B) compared to that in anatase, in spite of ca. three times smaller surface area of the former. Different charging mechanism explains facilitated Li-insertion in TiO_2(B). The difference is caused mainly by pseudocapacitive Li-storage in the bulk TiO_2(B). Deconvolution of cyclic voltammograms also indicates different capacitive contributions of the two voltammetric peaks, S1 and S2 of TiO_2(B). These results provide novel insight into the Li-storage in TiO_2(B) and its difference from that in anatase.

Acknowledgement: This work was supported by the Grant Agency of the Czech Republic (contracts No. 13-07724S, P108/12/0814 and 15-06511S).

1.Zachau-Christiansen, B.; West, K.; Jacobsen, T.; Atlung, S. *Solid State Ionics* **1988**, *28-30*, 1176.
2. Stashans, A.; Lunell, S.; Bergström, R.; Hagfeldt, A.; Lindquist, S. E. *Phys.Rev.B* **1996**, *53*, 159.
3.Wagemaker, M.; Lutzenkirchen-Hecht, D.; Van Well, A. A.; Frahm, R. *J.Phys.Chem.B* **2004**, *108*, 12456.
4.Armstrong, A. R.; Armstrong, G.; Canales, J.; Garcia, R.; Bruce, P. G. *Adv.Mater.* **2005**, *17*, 862.
5.Armstrong, G.; Armstrong, A. R.; Canales, J.; Bruce, P. G. *Electrochem.Solid State Lett.* **2006**, *9*, A139.
6.Armstrong, A. R.; Armstrong, G.; Canales, J.; Bruce, P. G. *J.Power Sources* **2005**, *146*, 501.
7. Zukalova, M.; Kalbac, M.; Kavan, L.; Exnar, I.; Graetzel, M. *Chem Mater* **2005**, *17*, 1248.
8. Laskova, B.; Zukalova, M.; Zukal, A.; Bousa,M.; Kavan, L. Journal of Power Sources 246 (2014) 103.

Does Modifying Electrodes *via* the Drop Casting Method Provide A Complete Coverage Over the Underlying Electrode Surface?

Ya Yun Chan, Alex Yong Sheng Eng, Martin Pumera and Richard D. Webster
Nanyang Technological University, Singapore
Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,
21 Nanyang Link, Singapore 637371
NEWRI-ECMG, Nanyang Environment and Water Research Institute, 1 Cleantech Loop, CleanTech One
#06-08, Singapore 637141
chan0660@ntu.edu.sg

Modifying electrodes with nanoscale carbonaceous materials for enhancing their performance is a widely used technique in electroanalytical chemistry applications [1]. Drop casting is a common approach as evidenced from the wide usage in literature reports. The coating procedure is usually assumed to cover the electrode completely but it is conceivable that the diffusion of the analyte within the electroactive pores of the nanomaterials all the way through to the base material may be occurring since drop cast layers are porous in nature. Cyclic voltammograms (CV) were recorded at 1 mm diameter copper (Cu) electrodes modified with porous layers of drop-coated multi-walled carbon nanotubes (MWCNTs) in the presence of aggressive SO_4^{2-} supporting electrolyte ions, where a large oxidative current indicated the occurrence of corroding Cu metal [2]. The layers were progressively built up on the electrode surface by depositing drop wise from 0 – 10 drops. It was demonstrated that a total of 10 drops of the coating solution (~ 640 μg/cm^2 of MWCNTs per unit area of electrode) was insufficient in providing a perfect coverage over the underlying electrode surface even though lesser loadings have been applied in the majority of literature reports. Scanning electron microscopy-energy dispersive X-ray spectroscopy did not detect Cu within a few hundreds of nanometers depth of the electrode surface although CV experiments clearly indicated events of Cu dissolution at the electrode with MWCNTs loading of 640 μg/cm^2. These results indicated that the drop casting procedure does not prevent access of the electroactive molecules to the base electrode material. It cannot be assumed that the base electrode, nor the pore structure of the coating material, does not significantly contribute to the observed voltammetric response.

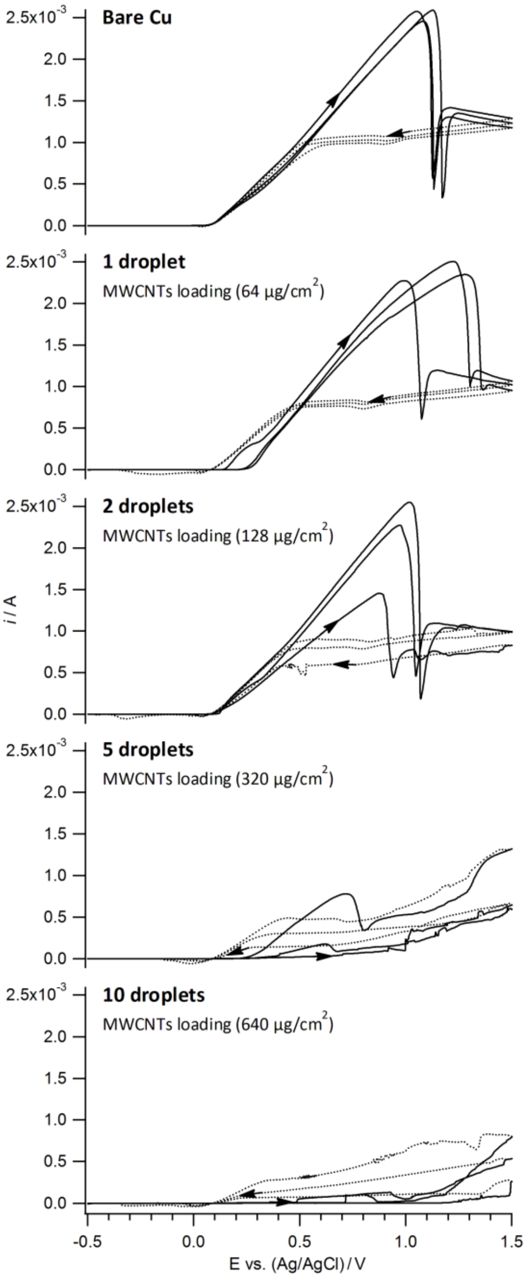


Fig. 1. Triplicate CVs (commencing at -0.5 V *vs.* Ag/AgCl) obtained at a scan rate of 2 mV s^{-1} at 1 mm diameter bare Cu and Cu electrodes modified with porous layers of MWCNTs from the drop casting solution in 0.1 M Na_2SO_4 solutions.

[1] L. Hu, D. S. Hecht, G. Gruner, Carbon Nanotube Thin Films: Fabrication, Properties and Applications, Chem. Rev. 110 (2010) 5790-5844.

[2] A. G. Christy, A. Lowe, V. Otieno-Alego, M. Stoll, R. D. Webster, Voltammetric and Raman microspectroscopic studies on artificial copper pits grown in simulated potable water, J. Appl. Electrochem. 34 (2004) 225-233.

A Discussion on the Water Treatment of Two-Phase Flow in the Membrane Electrode Assembly of PEMFCs

Ken-Ming Yin*, Hsiao-Kuo Hsuen, Yu-An Kung, Bo-Syun Cheng
Department of Chemical Engineering and Materials Science
135 Yuan Tung Road, Chung Li, Taoyuan, Taiwan 32003
**cekenyin@saturn.yzu.edu.tw*

Numerical simulation of two-phase flow is important for the performance evaluation of proton exchange membrane fuel cells (PEMFCs). Exchange of water between vapor and liquid phases in the gas diffusion layer (GDL) was considered by Nguyen and co-workers using the evaporation and condensation rate constants[1,2]. Such an approach has been widely employed by many researchers on the two-phase modeling of PEMFCs. Another two-phase flow approach was proposed by Hsuen and Yin, in which a pseudo-phase-equilibrium function is to approximate the vapor/liquid phase equilibrium[3]. Both methods predict species profiles in the GDL and cell performance at various degrees of inlet humidification without the need to determine liquid water front in the GDL explicitly. The present study compares the calculation consequence of these two approaches in detail. 1-D analytical solution based on the instantaneous equilibrium between two phases is used to verify the numerical predictions. The evaporation/condensation approach allows super-saturation near the cathode GDL and membrane interface. Thus, membrane is better hydrated near the interface after the emergence of liquid water as compared to the pseudo-phase equilibrium method. The ohmic resistance in Nguyen's prediction is less and better cell performance is obtained after liquid phase appears in the GDL.

References

[1] W. He, J. S. Yi, T. V. Nguyen, *AIChE J.*, 2000, 46, 2053-2064.
[2] D. Natarajan, T. V. Nguyen, *J. Electrochem. Soc.*, 2001, 148, A1324-1335.
[3] K. M. Yin, H. K. Hsuen, *Fuel Cells*, 2013, 13, 1213-1225.

Finite Element Modeling the Morphological Background to Capacity Fade in Si-Based Lithium-Ion Batteries

Shruti Srivastav, Chao- Xu, Kristina Edström, Daniel Brandell

Department of Chemistry-Ångström Laboratory, Uppsala University, Box 538, SE-75121, Sweden

shruti.srivastav@kemi.uu.se

Understanding the fundamental processes at the electrode/electrolyte interface during charge and discharge is a prerequisite for developing advanced Li-ion battery (LIB) systems with long lifetimes [1]. Interfacial reactions, which include lithium ion insertion/extraction, electrolyte decomposition, and the formation of a solid electrolyte interphase (SEI) layer, determine both irreversible capacity loss and cycle life of LIB systems [2,3]. Using Finite Element Methodology (FEM), the interplay between electrochemical performance and morphology changes can be investigated for a broad selection of electrode materials and properties.

In the current work, a 1D battery model generating repeated charge and discharge cycles is implemented for studying SEI layer growth and capacity loss when utilizing silicon (Si) as anode material in LIBs. Si possesses much higher capacities than the commercially used graphite anodes, but exhibits large volumetric expansion during Li intercalation [4]. This can result in cracking, subsequently leading to a detachment of the active material particles from each other and possibly also from the SEI layer film formed during previous cycles. The SEI layer will, due to continuous decomposition of electrolyte salt and solvent, cover the porous electrode surface, leading to a constant change in morphology and associated polarization during cycling. The continuous reformation of the SEI layer after each cycle also leads to a large consumption of Li in the battery cell. In comparison, the SEI film on traditional graphite anodes generally yield less capacity fade than on Si, although the chemical composition of the interface layers on the two materials appear similar [6,7]. In this context, Si-based LIB cells are here investigated theoretically to better understand the morphological background to the capacity fade using different electrolyte systems (see Fig. 1). Moreover, the simulation results are compared with experimental data from electrochemistry and X-ray Photoelectron Spectroscopy (XPS).

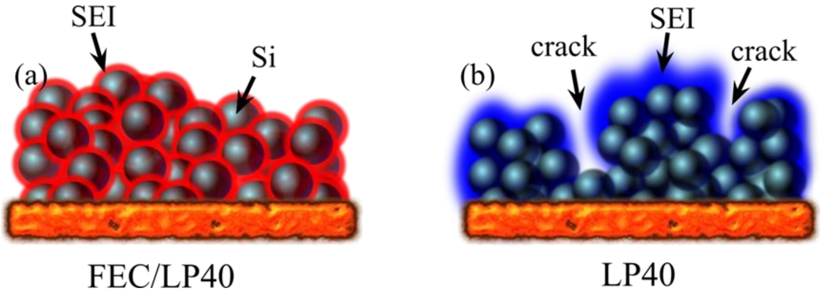


Fig. 1. Schematic representation of the SEI formation on a silicon anode after long-time cycling with FEC/LP40 (a) and LP40 (b) electrolytes, respectively.

References:

1) J. Newman and K. E. Thomas-Alyea, Electrochemical Systems, Third ed., Wiley Interscience, Berkeley (2004).
2) P. Ramadass, B. Haran, P. M. Gomadam, R. White, and B. N. Popov, J. Electrochem. Soc., 151, A196 (2004)
3) M. B. Pinson and M. Z. Bazant, J. Electrochem. Soc. 160, A243-A250 (2013).
4) X. Su , Q. Wu , J. Li , X. Xiao, A. Lott , W. Lu , B. W. Sheldon and J. Wu, Adv. Energy Mater. 2014, 4, 1300882.
5) J.-H. Cho and S. T. Picraux Nano Lett. 2014, 14, 3088−3095
6) P. B. Balbuena, Y. Wang, Lithium-Ion Batteries: Solid-Electrolyte Interphase; Imperial College Press: London, 2004.
7) K. Xu, Chem. Rev. 2004, 104, 4303−4417.

Relationship between the precipitation and electrochemical behavior of aluminum alloy type 2017A

S. BENAMIROUCHE[1]*, M.A. BELOUCHRANI [2], A. MERATI [2]
[1] *Laboratory of Electrochemistry and Corrosion, Military School Polytechnic, BP 17, 16046 - Algiers /Algeria.*
[2] *Office of Research and Development-Staff / ANP, Algiers/Algeria*
* *sofia_bene@yahoo.fr*

Abstract

This work is part of a global effort to understand the corrosion behavior of aluminum alloys of the 2000 series .Our study basically focuses on the temper of the studied materials, which is a key point for understanding the phenomena occurring corrosion.

As part of this work, an original approach was applied to study the electrochemical behavior of heat-treated alloys. For this, an experimental protocol was divided into two distinct categories. The first includes tests for analyzing the microstructures obtained after the various heat treatments and to identify the different phases of the material. The observational techniques used for this study are the Optical Microscopy and Scanning Electron Microscopy (SEM) .The electrochemical methods are also presented to increase their interest in the study of corrosion.

A good correlation was obtained between the various metal phases highlighted and the electrochemical behavior of these alloys in a chloride medium. The evolution of the microstructure according to the chemical composition was then revealed that the S- Al_2CuMg Phase played a major role. We met one type of corrosion is localized corrosion. Different forms of this type of corrosion encountered are galvanic corrosion, observed by a loosening of cathode particles and dissolution selective of anode particles. Galvanic coupling between the matrix and S- Al_2CuMg shows that the matrix passive and pinholes were observed on the S- Al_2CuMg phase, then, it is the second form that is intergranular corrosion.

T4 treatment with 20 days of aging has greater nobility, strength and low bias current of corrosion compared to the other treatments.

Key words

2017A, heat treatment, microstructure, precipitation, galvanic coupling.

Effect of Nanoparticles on the Efficiency of Aptasensors: A Comparative Study and the Aptamer of *E. coli* as a Model

Ezat Hamidi-Asl[a], Freddy Dardenne[b], Ronny Blust[b], Karolien De Wael[a]
[a]AXES Research Group, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
[b]Sphere Research Group, Department of Biology, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
Ezat.Hamidi-Asl@uantwerpen.be; freddy.dardenne@uantwerpen.be; ronny.blust@uantwerpen.be; karolien.dewael@uantwerpen.be

An electrochemical aptasensor based on carbon paste electrode (CPE) modified with different nanoparticles such as gold nanoparticles (Au), silver nanoparticles (Ag),hollow gold nanosphere (HGN), hollow silver nanosphere (HSN), silver-gold core:shell (Ag@Au), gold-silver core:shell (Au@Ag) and silver-gold alloy nanoparticles (Ag/Au) was developed. The main goal of this project was qualitative investigation of nanoparticles with different structures on the efficiency of aptasensor. No detailed information is available in the literature on the comparison between nanoparticles in aptasensing. Here, the aptamer for Escherichia coli (*E.coli*) bacteria was selected as a model. To prepare the modified CPE, the cysteamine was bound onto the surface of CPE by using cyclic voltammetry. Then, nanoparticles were self-assembled on the electrode via strong covalent bond to fabricate the nanoparticles self-assembled modified electrode. The morphology of the modified electrode was characterized with scanning electron microscopy. The electrochemical behavior of E.coli on the bare and modified CPE was investigated with cyclic voltammetry and differential pulse voltammetry in 0.1 M pH 6.0 phosphate buffer solution. Two well-defined oxidation peaks of E.coli on the bare CPE were obtained at + 0.81 V and + 0.95 V (vs. Ag/AgCl) that can be attributed to the oxidation of guanine. While after aptamer immobilization at the nanoparticle modified CPE, one peak appeared at + 0.95 V (vs. Ag/AgCl) that probably belongs to the synergic effects of nanoparticles and aptamer. The peak current of E.coli was linear with its concentration in the range of 1.0 to 10^{+6} CFU. To obtain optimized condition, further studies were done by Apt/Au/Cys/CPE including effect of different modified layer on nanoparticles adsorption, aptamer immobilization as well as selectivity of the aptasensor using other kinds of bacteria.