# Program of the

# 16<sup>th</sup> Topical Meeting of the International Society of Electrochemistry

Electrochemical Properties and Applications of Advanced Carbon Materials

> 22-26 March 2015 Angra dos Reis, Brazil

Organized by: Division 1 Analytical Electrochemistry Division 5 Electrochemical Process Engineering and Technology ISE Region Brazil Electrochemistry and Electroanalytical Division of the Brazilian Chemical Society



International Society of Electrochemistry Rue du Closelet 2 1006 Lausanne Switzerland

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## Program

# Table of Contents

Preliminary pages	i	- 1	vi
Sunday program		`	vi

#### Oral presentation program

Monday morning	1
Monday afternoon	
Tuesday morning	
Wednesday morning	
Wednesday afternoon	
Thursday morning	

#### Poster presentation program

Session 1	
Session 2	
Index	



## Sunday, 22 March 2015

18:00 - 19:30

## Welcome Reception Foyer of the Convention Center – 3rd floor

## Monday, 23 March 2015

08:30

## **Opening Ceremony**

Room: Centauro 2 & 3

## Monday, 23 March 2015, Morning

## **Keynote Lectures Session**

Room: Centauro 2 & 3

Chaired by Greg M. Swain

#### 08:40 to 09:40 Keynote

**Robert Hurt** (Department of Engineering, Brown University, Providence, USA) Modern Approaches to the Atomic-level Design of Functional Carbon Materials

#### 09:40 to 10:30 Keynote

**Rodney Ruoff** (IBS Center for Multidimensional Carbon Materials, Ulsan National Institute of Science and Technology, Ulsan, Korea) Novel Carbon and Related Materials

#### 10:30 to 10:50

Coffee Break

#### 10:50 to 11:40 Keynote

Christoph Nebel (Department of Sensors (GF5), Fraunhofer-Institute for Applied Solid State Physics, Freiburg, Germany), Fang Gao, Georgia Lewes-Malandrakis, Wolfgang Müller-Sebert

Diamond for electrochemical applications: From electrode arrays to diamond foam

#### 11:40 to 12:30 Keynote

Richard McCreery (Department of Chemistry, University of Alberta, Edmonton, Canada), Adam Bergren, Jerry Fereiro, Sayed Sayed, Bryan Szeto Carbon Electrodes for Molecular Electronics

## Monday, 23 March 2015, Afternoon

## Session 1

## Room: Centauro 1

Chaired by David J. Fermin and Claude Deslouis

#### 15:30 to 16:00 Invited

**David Fermin** (School of Chemistry, University of Bristol, Bristol, United Kingdom), Paul May, Hudson Zanin

High Surface Area Diamond Electrodes Templated by Vertically Aligned Carbon Nanotubes

#### 16:00 to 16:20

Federico Tasca (Departamento de Química de los Materiales, Universidad de Santiago de Chile, Santiago de Chile, Chile), Cristian Gutiérrez, F. Javier Recio, Ricardo Venegas, Marco Viera, Jose H. Zagal, César Zúñiga Catalytic Activity of MN4 Catalysts Adsorbed on Carbon Nanotubes Towards O<sub>2</sub> Reduction

#### 16:20 to 16:40

 Susana Córdoba de Torresi (Instituto de Quimica, Universidade de São Paulo, São Paulo, Brazil), Jadielson L. Antonio, Rafael N. P. Colombo, Vinicius R.
 Gonçales, Elaine Y. Matsubara, Marco A. de O. Minadeo, José M. Rosolen Free-standing Reduced Graphene Oxide Sheets Composites Supported onto 3D Matrix for different electrochemical applications

16:40 to 17:00 Coffee Break

## 17:00 to 17:30 Invited

**Claude Deslouis** (Laboratory Interfaces et Systèmes Electrochimiques UMR 8235, Univ. Paris VI, Paris, France)

Carbon Nitrides: Multipurpose Materials for Electrochemical Applications

## 17:30 to 17:50

Kateryna Artyushkova (Department of Chemical and Biological Engineering, University of New Mexico, Albuquerque, USA), Plamen Atanassov, Alexey Serov Role of carbon functionalization in oxygen reduction reaction

#### 17:50 to 18:10

**Fernando C. Moraes** (Department of Chemistry, Universidade Federal de São Carlos, São Carlos, Brazil), Angel Cuesta, Renato G. Freitas, Ernesto C. Pereira Electronic and Morphologic Changes in Graphene Oxide upon Electrochemical Reduction

## Session 2

## Room: Centauro 2

Chaired by Takeshi Watanabe and Carlos A. Martínez-Huitle

#### 15:30 to 16:00 Invited

**Takeshi Watanabe** (Department of Chemistry, Keio University, Yokohama, Japan), Yasuaki Einaga

Electrochemical Applications of Conductive Diamond Electrodes and the Tailored Design for the Applications

#### 16:00 to 16:20

David Tatsuo Atique Sawazaki (Department of Chemistry, Faculty of Philosophy, Science and Letters of Ribeirao Preto - USP, Ribeirão Preto, Brazil), Zeki Naal, Edgar Suzuki

Functionalization of Graphite in Friedel-Crafts Reaction Condition: Electrochemical Characterization and Aging

#### 16:20 to 16:40

**Thomas Rabbow** (F&E, Cellstrom GmbH, Wiener Neudorf, Austria), Paul Binder, Peter Pokorny, Markus Trampert, Adam Whitehead

The reproducibility of properties of PAN-based graphite fibres after thermal treatment

16:40 to 17:00 Coffee Break

#### 17:00 to 17:30 Invited

**Carlos Alberto Martínez-Huitle** (Institute of Chemistry, Federal University of Rio Grande do Norte, Natal, Brazil), Djalma R. da Silva, Danyelle M. de Araújo, Chrystiane do Nascimento Brito, Manuel Andres Rodrigo Studying the effect of sp<sup>3</sup>/sp<sup>2</sup> ratio on electrochemical oxidation and production of oxidant species using boron doped diamond films

#### 17:30 to 17:50

Zhirong Lin (School of Environment, Tsinghua University, Beijing, China), Shi Yuan, Huijiao Wang, Xiang Li, Yujue Wang

Inhibition of chlorate and perchlorate formation during clofibric acid degradation by electro-peroxone process

## 17:50 to 18:10

Luca Pujol (Laboratoire de Génie Chimique, Université Paul Sabatier, Toulouse, France), David Evrard, Mathilde Freyssinier, Karine Groenen-Serrano, Pierre Gros, Audrey Ruffien-Ciszak

Potentialities of a boron-doped diamond substrate for a two-step electrochemical process including sample mineralization and lead(II) assay in synthetic and real media

#### 18:10 to 19:40

Room Brisa 2/3

Poster Presentation Session Discussion of odd-numbered posters

4

## Tuesday, 24 March 2015, Morning

## Session 1

## Room: Centauro 1

Chaired by Vadym N. Mochalin and François Béguin

#### 08:30 to 09:00 Invited

**Vadym Mochalin** (Department of Materials Science and Engineering, Drexel University, Philadelphia, USA), Yury Gogotsi

Onion-like Nanocarbon and MXenes for Electrochemical Energy Storage Applications

#### 09:00 to 09:20

Krzysztof Fic (Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland), Elzbieta Frackowiak, Mikolaj Meller Electrosorption on Carbon for Hybrid Aqueous Supercapacitors

#### 09:20 to 09:40

Abdulhakeem Bello (Department of Physics, University of Pretoria, Hatfield, South Africa), Farshad Barzegar, Kouadio Julien Dangbegnon, Ncholu Manyala, Damilola Momodu, Fatemeh Taghizadeh

Production of porous carbons based on graphene foam-PVA/phenol-formaldehyde composite as electrode material for supercapacitors

#### 09:40 to 10:00

Pawel Jezowski (Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland), François Béguin, Thierry Brousse, Olivier Crosnier, Krzysztof Fic

New pre-lithiation strategies of the graphite anode in lithium-ion capacitors

#### 10:00 to 10:20

Alar Jänes (University of Tartu, Institute of Chemistry, Tartu, Estonia), Jaanus Eskusson, Enn Lust, Thomas Thomberg

Specific Electrolyte Additives for Non-Aqueous Carbon-based Supercapacitors

10:20 to 10:40 Coffee Break

#### 10:40 to 11:10 Invited

**François Béguin** (Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland), Qamar Abbas, Paulina Babuchowka, Paula Ratajczak

Development of a high energy AC/AC capacitor in aqueous electrolyte

#### 11:10 to 11:30

Victor Hugo R. de Souza (Department of Chemistry, Universidade Federal do Paraná (UFPR), Curitiba, Brazil), Marcela M. Oliveira, Aldo J.G. Zarbin Flexible and all-solid supercapacitor based on carbon nanotubes/ polyaniline nanocomposite films

#### 11:30 to 11:50

Sergej Rothermel (MEET Battery Research Center, University of Muenster, Münster, Germany), Martin Grützke, Sascha Nowak, Martin Winter Treatment and Electrochemical Performance of Recycled Graphite from Spent Li-Ion Batteries

#### 11:50 to 12:10

Enn Lust (Institute of Chemistry, University of Tartu, Tartu, Estonia), Jaanus Eskusson, Alar Jänes, Rait Kanarbik, Heisi Kurig, Ann Laheäär, Priit Möller, Rasmus Palm, Indrek Tallo, Ester Tee

Electrochemical Behavior of Hybrid Devices Based on Alkaline Metal Salts in Neutral Aqueous and Non-Aqueous Electrolytes and Carbon Electrodes within Very Wide Cell Potential Region

13:30 - 18:00

## Excursions

## Session 2

## Room: Centauro 2

Chaired by Christopher M.A. Brett and Lauro T. Kubota

#### 08:30 to 09:00 Invited

Christopher Brett (Department of Chemistry, Faculty of Science and Technology, University of Coimbra, Coimbra, Portugal), Madalina Barsan, Mariana Emilia Ghica, Carla Gouveia-Caridade

Carbon Nanotubes for Novel Electrochemical Sensing Applications

#### 09:00 to 09:20

Barbara Kowalewska (Department of Chemistry, University of Warsan, Warsan, Poland), Adrian Patyna

Application of Electrochemically and Chemically Reduced Graphene Oxide Noncovalently Modified with Tetrathiafulvalene for Glucose Biosensing

#### 09:20 to 09:40

**Omolola E. Fayemi** (Department of Mathemathics and Physical Sciences, North-West University, Mafikeng, South Africa), Abolanle S. Adekunle, Eno E. Ebenso A Sensor for Determination of Serotonin in Human Urine using a Multi-Walled Carbon Nanotube/Ni, Zn and Fe Oxides Composites Modified Glassy Carbon Electrode

#### 09:40 to 10:00

**Ilanna C. Lopes** (Departamento de Quimica, Universidade Federal do Maranhao, São Luis, Brazil), Thaylan P. Araujo, Adriana P. Rodrigues, Sonia Maria C. N. Tanaka, Auro A. Tanaka

Carboxylated  $\beta$ -Cyclodextrin-reduced Graphene Oxide for the Voltammetric Determination of Diuron Herbicide

#### 10:00 to 10:20

**Umit Demir** (Department of Chemistry, Atatürk University, Erzurum, Turkey), Tuba Oznülüer, Hülya Oztürk Dogan

Layer-by-Layer Electrochemical Fabrication of Reduced Graphene Oxide-Metal/Metal Oxide Nanocomposites for Catalyst and Sensor Applications

10:20 to 10:40 Coffee Break

#### 10:40 to 11:10 Invited

Lauro Kubota (Department of Analytical Chemistry, Unicamp, Campinas, Brazil), Maiui Camargo, Camila Maroneze, Murilo Santhiago, Cecilia Silva Electroanalytical Devices Based on Carbon Nanotubes, Reduced Graphene Oxide and Graphene

#### 11:10 to 11:30

Andreas Lesch (Laboratoire d'Electrochimie Physique et Analytique, École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland), Véronique Amstutz, Fernando Cortés-Salazar, Hubert H. Girault, Philippe Tacchini

Nano-Hydrogel/Carbon Nanotubes Electrodes For Matrix Independent Sensing

#### 11:30 to 11:50

**Eva Menart** (Department of Analytical Chemistry Laboratory, National Institutue of Chemistry, Ljubljana, Slovenia), Samo B. Hoèevar, Vasko Jovanovski, Janez Kovaè, Bozidar Ogorevc

*In-situ* electrochemical preparation of graphene electrodes in various ionic liquids and potential electroanalytical applications

#### 11:50 to 12:10

Paolo Bertoncello (Department of Engineering, Swansea University, Swansea, United Kingdom), Thomas Jones, Robert Kaspar, Michael Letterio, Andrea Notargiacomo, Marialilia Pea, Delia Puzzovio, Yushan Yan

Nanostructured Conductive Anion Exchange (TPQPOH) Ultra-Thin Langmuir-Schaefer films for Electrocatalytic Application

13:30 - 18:00

## Excursions

## Wednesday, 25 March 2015, Morning

## Session 1

## Room: Centauro 1

Chaired by Dirk M. Guldi and Daniel Bélanger

#### 08:30 to 09:00 Invited

**Dirk Guldi** (Department of Chemistry and Pharmacy, University of Erlangen, Erlangen, Germany)

Nanocarbons for optoelectronic applications

#### 09:00 to 09:20

Alain Pailleret (Labo. Interfaces et Systèmes Electrochimiques (UMR 8235), University Pierre and Marie Curie, Paris, France), Florence Billon, Joshua C. Byers, Claude Deslouis, Oleg A. Semenikhin

Electronic Properties and Morphological Characteristics of Carbon Nitride/Conjugated Polymer Composite Materials Aimed at Photocurrent Generation

#### 09:20 to 09:40

Tharamani C. Nagaiah (Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar, India), Wolfgang Schuhmann, Chen Jin, Martin Muhler

Electrocatalytic oxidation of methanol at PtRu nanoparticles supported on nitrogen doped carbon nanotubes

#### 09:40 to 10:00

Rakesh Kumar (Department of Chemistry, National University of Ireland, Galway, Galway, Ireland), Paul Kavanagh, Dónal Leech, Isioma Osadebe, Peter O'Conghaile

Glucose oxidizing anodes under physiological conditions: Using design of experiment to probe optimum combination of enzyme, mediator and support materials

#### 10:00 to 10:20

Wei-Nien Su (Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, Taiwan), Abiye Kebede Agegnehu, Amare Aregahegn Dubale, Bing-Joe Hwang, Jyh-Fu Lee, Chun-Jern Pan, Andebet Gedamu Tamirat

Reduced graphene oxide modified nanocomposites for solar water splitting

#### 10:20 to 10:40

Coffee Break

#### 10:40 to 11:10 Invited

**Daniel Bélanger** (Department of Chemistry, Université du Quebec à Montreal (UQAM), Montreal, Canada), Thierry Brousse, Annaïg Le Comte

Chemically functionalized carbons for application in energy storage systems

#### 11:10 to 11:30

Rutha Jäger (Institute of Chemistry, University of Tartu, Tartu, Estonia), Eneli Härk, Enn Lust, Tavo Romann

Kinetics of the Oxygen Electroreduction at Carbon-supported Noble and Non-noble Metal Nanoparticles Activated Electrodes

#### 11:30 to 11:50

Nasser A. M. Barakat (Department of Organic Materials and Fiber Engineering, Chonbuk National University, Jeonju, Korea), Mohammad Abdelkareem, Khalil Khalil, Moaaed Motlak

CoNi-loaded graphene as effective non-precious electrocatalyst for methanol oxidation in alkaline medium

#### 11:50 to 12:10

Ladislav Kavan (Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic), Jan Barton, Petr Cigler, Hana Krysova, Milos Nesladek, Vaclav Petrak, Zuzana Vlckova-Zivcova

Boron-doped Diamond Electrode: Spectro/Photo/Electrochemistry and Prospective Application in Dye-sensitized Solar Cell

## Session 2

## Room: Centauro 2

Chaired by Craig M. Banks and Greg M. Swain

#### 08:30 to 09:00 Invited

**Craig Banks** (Department of Chemistry, Manchester Met Uni, Manchester, United Kingdom)

Electrochemical Explorations of Graphene and Related Materials

#### 09:00 to 09:20

Roberto Torresi (Instituto de Química, Universidade de São Paulo, São Paulo, Brazil), Lucas Lodovico, José Maurício Rosolen, Elaine Yoshiko Matsubara Electrochemistry of graphene deposited by different methods

#### 09:20 to 09:40

**Matej Velicky** (School of Chemistry, University of Manchester, Manchester, United Kingdom), Robert Dryfe Electron Transfer Kinetics on Graphene

#### 09:40 to 10:00

Samantha Husmann (Department of Chemistry, Universidade Federal do Paraná, Curitiba, Brazil), Aldo J. G. Zarbin

Carbon Nanotubes/Prussian Blue Analogues Thin Films Nanocomposites: Multifunctional Materials

#### 10:00 to 10:20

Pierre Millet (Department of Chemistry, Université Paris-Sud, Orsay, France), Anuradha Ragupathy, Alireza Ranjbari, Angel Villagra

Implementation of metallic clathrochelates at the surface of carbonaceous substrates for hydrogen evolution in acidic media

#### 10:20 to 10:40

Coffee Break

#### 10:40 to 11:10 Invited

**Greg Swain** (Department of Chemistry, Michigan State University, East Lansing, USA), Romana Jarosova, Catherine Munson

The Electrochemical Properties of Diamond and Tetrahedral Amorphous Carbon Electrodes in Room Temperature Ionic Liquids

#### 11:10 to 11:30

Ana Maria Oliveira-Brett (Chemistry Department, University of Coimbra, Coimbra, Portugal), T. Adrian Enache, S. Carlos B. Oliveira

Hydroxyl Radicals Electrochemically Generated *in Situ* at a Borondoped Diamond Electrode Surface: Interaction with Biological Compounds

### 11:30 to 11:50

Lo Gorton (Dept. of Biochemistry and Structural Biology, Lund University, Lund, Sweden), Hans-Erik Akerlund, Per-Åke Albertsson, Huseyin Bekir Yildiz, Sinan Cem Emek, Yusuf Dilgin, Cecilia Hägerhäll, Kamrul Hassan, Dónal Leech, Peter O'Conghaile, Michael A. Packer, Eva Sperling

Electrochemical Communication between Bacterial Cells/Biological Membranes and Carbon Electrodes

#### 11:50 to 12:10

Nicky Mac Kenna (Chemical Sciences, Dublin City University, Dublin, Ireland), Paul Calvert, Aoife Morrin, Simon E. Moulton, Gordon G. Wallace Electrically Controlled Drug Delivery from a Reduced Graphene Oxide Composite Hydrogel

## Wednesday, 25 March 2015, Afternoon

## Session 1

## Room: Centauro 1

Chaired by Alison J. Downard and Manuel A. Rodrigo

#### 15:30 to 16:00 Invited

Alison Downard (Department of Chemistry, University of Canterbury, Christchurch, New Zealand), Paula Brooksby, Simon Brown, Anna Farquhar, Philippe Hapiot, Lita Lee, Yann Leroux, Haifeng Ma Modification of Edge and Basal Plane Graphitic Carbon using Aryldiazonium Salts: Chemisorption vs Physisorption

#### 16:00 to 16:20

Viatcheslav Jouikov (UMR 6226, Molecular Chemistry and Photonics, University of Rennes, Rennes, France), Jacques Simonet Functionalization of Macroscopic Carbon Materials Electrochemically Inducing Their Polyaromatic Reactivity

#### 16:20 to 16:40

**Eduardo G. C. Neiva** (Department of Chemistry, Universidade Federal do Paraná, Curitiba, Brazil), Luiz H. Marcolino Jr., Aldo J. G. Zarbin Synthesis and Characterization of Graphene/Ni(OH)<sub>2</sub> Nanocomposites Obtained by Polyol Method and Electrochemical Characterization in Alkaline Medium

#### 16:40 to 17:00

Coffee Break

#### 17:00 to 17:30 Invited

Manuel Andres Rodrigo (Department of Chemical Engineering, Universidad de Castilla-la-Mancha, Ciudad Real, Spain), Pablo Cañizares, Salvador Cotillas, Javier Llanos, María José Martín de Vidales, Jose Fernando Pérez-Serrano, Cristina Sáez

Diamond anodes for electrolysis of wastewater: Key material or fake?

#### 17:30 to 17:50

Marcos Lanza (DQFM, IQSC / USP, São Carlos, Brazil), Willyam Barros, Rodnei Bertazzoli, Jussara Carneiro, Marcos Lanza, Geiser Oliveira, Jonas Reis, Robson Rocha, Mauro Santos, Fernando Silva, Leandro Trevelin, Ricardo Valim, Marcelo Zaiat

Electrochemical production of hydrogen peroxide: Since the study of oxygen reaction reduction until  $\rm H_2O_2$  generation in electrochemical flow reactor

## 17:50 to 18:10

Khalil Abdelrazek (Mechanical Engineering Department, College of Engineering, King Saud University, Riyadh, Saudi Arabia), Nasser A. M. Barakat, Ahmed G. El-Deen

Tin oxide/graphene nanocomposite as an effective electrode material for capacitive deionization technology

## Session 2

## Room: Centauro 2

Chaired by Osamu Niwa and Orlando Fatibello-Filho

## 15:30 to 16:00 Invited

**Osamu Niwa** (Biomedical Research Institute, National Institute of Advanced Industrial Sci. and Tech., Tsukuba, Japan), Shigeru Hirono, Tomoyuki Kamata, Dai Kato, Masashi Kunitake, Eisuke Kuraya

Electrochemical properties of surface terminated and hybrid carbon films and their application to electroanalysis

## 16:00 to 16:20

Eric Gil (Faculty of Pharmacy, Federal University of Goias, Goiania, Brazil), Stephen Benjamin, Luane Garcia, Jhéssica Golveia, Flavio Lopes, Mariangela Santiago

Carbon paste based biosensors for antioxidant capacity

#### 16:20 to 16:40

**Emiliano Primo** (INFIQC-Departamento de Físicoquimica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina), Marcos Eguílaz, Nancy Ferreryra, Aurelien Gasnier, Fabiana Andrea Gutierrez, Alejandro Gutiérrez, Guillermina Luque, María Pedano, Gustavo Rivas, Marcela Rodríguez, María Rubianes

Electrochemical (bio)sensors based on the use of carbon nanomaterials

#### 16:40 to 17:00

Coffee Break

#### 17:00 to 17:30 Invited

**Orlando Fatibello-Filho** (Department of Chemistry, São Carlos Federal University, São Carlos, Brazil)

Use of Electrochemically Pretreated Boron-doped Diamond Electrodes in Electroanalytical Methods

#### 17:30 to 17:50

Ntsoaki Mphuthi (Department of Chemistry, North West University, Mafikeng, South Africa), Abolanle S. Adekunle, Eno E. Ebenso

Electrochemical Study of Dopamine at Metal Oxide-doped Phthalocyanine supported on Carbon Nanotubes Modified Glassy Carbon Electrode Platform

#### 17:50 to 18:10

Abdulkadir Sanli (Faculty of Electrical Engineering and Information Technology, Technische Universität Chemnitz, Chemnitz, Germany), Abderrahmane Benchirouf, Olfa Kanoun, Christian Müller, Abhimanyu Das Thakur Impedance Characterization of Multiwalled Carbon Nanotubes-Polymer-based Flexible Thin Film Piezoresistive Strain Sensors

#### 18:10 to 19:40

Room Brisa 2/3

Poster Presentation Session Discussion of even-numbered posters

20:30 - 23:30

## **Farewell Dinner**

Ballroom Enseadas (Convention Center - 2nd floor)

# Thursday, 26 March 2015, Morning

## Session 1

## Room: Centauro 1

Chaired by Bing-Joe Hwang and Pasquale F. Fulvio

## 08:30 to 09:00 Invited

**Bing-Joe Hwang** (Department of Chem. Eng., National Taiwan University of Science and Technology, Taipei, Taiwan)

Superior Capacitance Behavior of Stacking Free Graphene Prepared by Glucose-assisted Freeze-drying Process

#### 09:00 to 09:20

Elzbieta Frackowiak (Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poznan, Poland), François Béguin, Piotr Skowron

The Carbon/Iodide Interface in Protic Ionic Liquid for Capacitors

## 09:20 to 09:40

Eneli Härk (Institute of Chemistry, University of Tartu, Tartu, Estonia), Rutha Jäger, Enn Lust

Optimization of the binder concentration in the hierarchically microporous – mesoporous carbon catalyst layer

## 09:40 to 10:00

Pasquale Fulvio (Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico), Sheng Dai, Xiqing Wang, Richard T. Mayes, Shannon M. Mahurin, Bingkun Guo, Xiao-Guang Sun, Alex A. Puretzky, Christopher M. Rouleau, David B. Geohegan

Tailoring the electronic conductivity in "brick and mortar" ordered mesoporous carbon – graphitic carbon nanostructures supercapacitor electrodes

#### 10:00 to 10:20

**Ozlem Sel** (Laboratoire LISE (Interfaces et Systèmes Electrochimiques), Sorbonne Universités UPMC Univ. Paris 06, Paris, France), Abdelkrim El Kadib, Freddy Escobar, Hamza Goubaa, Mohammed Lahcini, Ivan T. Lucas, Hubert Perrot, Mustapha Raihane, Ibtissam Ressam

Capacitive Charge Storage Behavior of Electrochemically Reduced Graphene Oxides Investigated by Fast Electrogravimetric Methods

#### 10:20 to 10:40

Coffee Break

#### 10:40 to 11:00

**Ditty Dixon** (Institute for Applied Materials, Energy Storage Systems, Karlsruhe Institute of Technology, Karlsruhe, Germany)

Oxygen plasma treated carbon electrodes for redox flow batteries

#### 11:00 to 11:20

Petr Mazur (New Technologies, Research Centre, University of West Bohemia, Plzen, Czech Republic), Jan Dundalek, Juraj Kosek, Jaromir Pocedic, Jiri Vrana

Electrochemical preparation of graphene-modified carbon felt electrodes for vanadium redox flow battery

#### 11:20 to 11:40

Kan-Hao Xue (Laboratoire de Réactivité et Chimie des Solides, Université de Picardie Jules Verne, Amiens, France), Alejandro A. Franco, Claude Guery, Mathieu Morcrette

Multiscale Modeling of Lithium Sulfur Battery Involving Cathode Carbon Microstructure

#### 11:40 to 12:00

**Tiphaine Poux** (*Electrochemistry Laboratory - Energy Storage, Paul Scherrer Institut, Villigen PSI, Switzerland*), Dario Cericola, Juan Luis Gómez-Cámer, Thomas Hucke, Petr Novák, Michael E. Spahr

Increasing the Life Time of Si/C Composite Electrodes for Lithium-Ion Batteries

## Session 2

## Room: Centauro 2

Chaired by Enric Brillas and Luiz H. Dall'Antonia

## 08:30 to 09:00 Invited

Enric Brillas (Química Física, Universitat de Barcelona, Barcelona, Spain) Degradation of Organic Pollutants from Waters Using Electrochemical Advanced Oxidation Processes with a Boron-doped Diamond Anode

## 09:00 to 09:20

Xiang Li (School of Environment, Tsinghua University, Beijing, China), Yu Jue Wang, Gang Yu

Degradation of the antidepressant venlafaxine by electro-peroxone process

## 09:20 to 09:40

Monica Cerro-Lopez (Chemical and Biological Sciences, Fundación Universidad de las Américas-Puebla, Puebla, Mexico), Alejandra Garcia-Garcia, Abraham Mauleon Amieva, Yunny Meas-Vong, Marco A. Quiroz

Synthesis, Characterization and Photoelectrochemical Performance of Hybrid Electrodes Based on Titania Nanotubes and Reduced Graphite Oxide

## 09:40 to 10:00

Luiz Henrique Dall Antonia (Departamento de Quimica, Universidade Estadual de Londrina, Londrina, Brazil), Vanildo Souza Leão Neto Synthesis and characterization of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/reduce graphene oxide electrodes for application in photoelectrocatalysis

## 10:00 to 10:20

**Neemias Cintra Fernandes** (Department of Chemistry, Instituto Federal de Goiás, Goiânia, Brazil), Eric de Souza Gil, Luane Ferreira Garcia, Fernando Miguel de Amorim Lino, Jerônimo Raimundo de Oliveira Neto

Development of C -  $\mathrm{TiO}_2$  electrodes obtained by compression

## 10:20 to 10:40

Coffee Break

18

#### 10:40 to 11:00

Ernesto Calvo (INQUIMAE, CONICET, Universidad de Buenos Aires, Buenos Aires, Argentina), Maria del Pozo Vazquez, Santiago Herrera, Florencia Marchini, Nataliia Mozhzhukhina, Alvaro Tesio, Walter Torres, Federico Williams

Electrochemical and Spectroscopic Studies of Carbon Cathodes for Oxygen Reduction in DMSO Lithium Electrolytes

## 11:00 to 11:20

Nick Daems (Centre for Surface Chemistry and Catalysis, K.U. Leuven, Heverlee, Belgium), Annick Hubin, Paolo Pescarmona, Patrick Steegstra, Ivo Vankelecom

N-doped graphitic carbons as electrocatalysts for the synthesis of hydroxylamine with cogeneration of electricity

## 11:20 to 11:40

Tsuyoshi Ochiai (Photocatalyst Group, Kanagawa Academy of Science and Technology, Kawasaki, Japan), Akira Fujishima, Mio Hayashi, Kazuo Hirota, Takeshi Kondo, Kazuhito Satomura, Shoko Tago

Flexible Pinpoint Electrolysis Unit Coated with Boron-doped Diamond Powder (BDDP) Based Polymer Composites for Dental Treatments

## 11:40 to 12:00

**Andrew Rodgers** (School of Chemistry, University of Manchester, Manchester, United Kingdom), Robert Dryfe

Interfacial Adsorption and Catalysis using Few-layer Graphene

## Monday 18:10 to 19:40

Poster Presentation Session

discussion of odd-numbered posters

## Wednesday 18:10 to 19:40

## **Poster Presentation Session**

discussion of even-numbered posters

## **Poster Presentations**

## Session 1

## Room: Brisa 2/3

#### s1-001

Alejandro Alvarez-Lueje (Pharmacological and Toxicological Chemistry, University of Chile, Santiago, Chile), Viviana Moncada, Bárbara Pérez, Patricia Pizarro

Carbon-based Electrodes Modified with Ionic Liquids for Drug Analysis

#### s1-002

Joseany de Moraes Santos Ameida (Department of Chemistry, Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro, Brazil), Ricardo Queiroz Aucélio, Rafael Dornellas

Voltammetric determination of trifloxystrobin in orange juice and water samples using the boron-doped diamond electrode

## s1-003

Vilma Araujo da Costa (Department of Materials, UFRN, Natal, Brazil), Danyelle M. de Araújo, Carlos Alberto Martínez-Huitle, Sibele B. C. Pergher

Electroreduction of nitrate using diamond films and different cathodes

## s1-004

Lorena Athie Goulart (Chemistry Department, Universidade Federal de São Carlos, São Carlos, Brazil), Lucia Mascaro

Electrochemical Detection of Bisphenol A at a Carbon Nanotubes-NiO Nanoparticles Electrode

## s1-005

Nerilso Bocchi (Department of Chemistry, São Carlos Federal University, São Carlos, Brazil), Sonia R. Biaggio, Regina V. Oliveira, Gabriel F. Pereira, Romeu C. Rocha-Filho, Bianca F. da Silva

Direct and Indirect Electrochemical Degradation of Tebuthiuron Using a Boron-doped Diamond Anode in a Flow System

Ricardo Brocenschi (Department of Chemistry, São Carlos Federal University, São Carlos, Brazil), Kallyni Irikura, Romeu C. Rocha-Filho, Naihara Wächter Electrochemical Surface Rehydrogenation of Boron-doped Diamond Electrodes After an Electrochemical Polishing Process

## s1-007

Ricardo Brocenschi (Department of Chemistry, São Carlos Federal University, São Carlos, Brazil), Sonia R. Biaggio, Nerilso Bocchi, Bianca F. da Silva, Romeu C. Rocha-Filho

The Influence of the Electrolyte pH on the Mechanism of Electrodegradation of Estrone in a Flow Reactor Using a Boron-doped Diamond Anode

## s1-008

**Rafael Cardoso** (Institute of Chemistry, Federal University of Uberlandia, Uberlandia, Brazil), Eduardo Almeida, Rafael Dornellas, Rodrigo Montes, Rodrigo Munoz, Edson Nossol, Eduardo Richter

The effect of multi-walled carbon nanotube dimensions on the electrochemical oxidation of phenolic compounds

## s1-009

Rongzhi Chen (Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan), Miyuki Asai, Chikako Fukushima, Tohru Kawamoto, Hisashi Tanaka, Yuanxun Zhang Preparation and modification of 3-D nanostructure film of MHCF for electrochemical separation of cesium

## s1-010

Victor Costa Bassetto (EDCH, École Polytechnique Fédérale de Lausanne -EPFL, Lausanne, Switzerland), Alexandra Bondarenko, Fernando Cortés Salazar, Hubert Girault, Sunny Isaïe Maye, Andreas Lesch

Inkjet Printed Carbon Nanotubes Electrodes for Environmental Sensing

## s1-011

Andrea Couto (LAS, Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Brazil), Mauricio Baldan, Neidenei Ferreira, Fernanda Migliorini Electrocatalytic Oxidation of Organic Contaminants Using TiO<sub>2</sub>/ BDD/Ti Composite Electrode

Rogério A. Davoglio (Department of Chemistry, Federal University of São Carlos, São Carlos, Brazil), Sonia R. Biaggio, Nerilso Bocchi, Romeu C. Rocha-Filho

Production of Electrolytic Manganese Dioxide on Boron-doped Diamond for Use in Lithium Batteries

#### s1-013

Rodrigo del Rio (Departamento de Quimica Inorganica, Facultad de Quimica, Pontificia Universidad Catolica de Chile, Santiago, Chile), Camila Araneda, Francisco Armijo, Daniel Correa, Maria Jose Rubio

Electrochemical Degradation of Phthalates Using Boron-doped Diamond Electrode

#### s1-014

Patricio Javier Espinoza-Montero (Department of Engineering, Escuela Politécnica Nacional, Quito, Ecuador), Benardo Frontana-Uribe, Jorge G. Ibanez, Ruben Vasquez-Medrano

Efficient Anodic Degradation of Phenol Paired to Improved Cathodic Production of H<sub>2</sub>O<sub>2</sub> at BDD Electrodes

## s1-015

**Orlando Fatibello-Filho** (Department of Chemistry, São Carlos Federal University, São Carlos, Brazil), Evaldo Corat, Paul May, Tiago Silva, Hudson Zanin

Exploring the Electroanalytical Performance of Porous Diamond-Like Carbon Electrodes Grown on Vertically Aligned Carbon Nanotubes

## s1-016

Neidenei Gomes Ferreira (LAS, Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Brazil), Mauricio Baldan, Marcos Lanza, Fernanda Migliorini

Electrooxidation of the Textile Dye Using Boron-doped Diamond Electrodes with Different Doping Levels and sp<sup>2</sup> Content

Neidenei Gomes Ferreira (Laboratorio Associado de Sensores e Materials, Instituto Nacional de Pesquisas Espaciais, São Jose dos Campos, Brazil), Dalva Alves de Lima Almeida, Mayara Camila Duarte de Oliveira, Carla Polo Fonseca, Maurício Ribeiro Baldan

Synthesis and Characterization of PAni/CNT/CF Composites: Morphological, Structural and Electrochemical Analyses

## s1-018

**Caroline Gomes** (Department of Fundamental Chemistry, University of São Paulo, São Paulo, Brazil), Rafael Buoro, Othon S. Campos, Silvia Serrano Evaluation of BDDE surface pre-treatment towards the oxidation of indolic compounds

#### s1-019

Fabiana Andrea Gutierrez (Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Cordoba, Argentina), Soledad Bollo, Pilar Herrasti, Eva Mazario, Javier Recio, Gustavo A. Rivas, M.Dolores Rubianes, Jose H. Zagal

Catalytic Activity Towards H<sub>2</sub>O<sub>2</sub> Reduction of Carbon Composites Containing MFe2O4 Nanoparticles

## s1-020

Kallyni Irikura (Department of Chemistry, Federal University of São Carlos, São Carlos, Brazil), Romeu C. Rocha-Filho, Orlando Fatibello Filho, Greg M. Swain

Effect of Anodic and Cathodic Pretreatment on the Electrochemical Activity of Boron-doped Diamond Electrodes from Different Sources

## s1-021

Katarzyna Jakubow (Department of Chemistry, University of Warsan, Warsan, Poland), Barbara Kowalewska

Ethanol Sensing and Direct Electrochemistry of Adsorbed Alcohol Oxidase on 4-(pyrrole-1-yl) Benzoic Acid Functionalized Carbon Nanotubes

#### s1-022

Katarzyna Jakubow (Department of Chemistry, University of Warsan, Warsan, Poland), Barbara Kowalewska

Comparative Studies on Impact of Immobilization Method on Direct Electron Transfer of Glucose Oxidase Adsorbed on 4-(pyrrole-1-yl) Benzoic Acid Modified Carbon Nanotubes

25

#### s1-023

**Paola Jara-Ulloa** (Ciencias Químicas, Universidad Andres Bello, Santiago, Chile), S. Catalán-Caro

Electrochemical detection of copper using glassy carbon electrodes modified with multiwalled carbon nanotubes

### s1-024

Fabio S. Lisboa (Department of Chemistry, University of Parana, Curitiba, Brazil), Marcio Bergamini, Luiz Humberto Marcolino Jr., Aldo J. G. Zarbin Nanocomposite of Polyaniline and Multiwalled Carbon Nanotubes for Use as Optical and Electrochemical Sensor

## s1-025

Ilanna C. Lopes (Departamento de Quimica, Universidade Federal do Maranhao, São Luis, Brazil), Josimar A. Araujo, Thaylan P. Araujo, Iranaldo S. Silva, Sonia Maria C. N. Tanaka, Auro A. Tanaka

Triclosan Detection on a Molecularly Imprinted Carbon Nanotube Sensor

#### s1-027

Rafael Machado Dornellas (Instituto de Química, Universidade Federal de Uberlândia, Uberlândia, Brazil), Rodrigo Alejandro Abarza Muñoz, Ricardo Queiroz Aucélio

Electrochemical determination of picoxystrobin on boron-doped diamond electrode: Square-wave voltammetry vs. BIA-amperometry

## s1-028

Lucia Mascaro (Department of Chemistry, Universidade Federal de São Carlos, São Carlos, Brazil), Fernando C. Moraes, F. Willian de S. Lucas

Development of Ti/TiO<sub>2</sub>/CNTs Films to Use as Cathode for Hydrogen Evolution Reaction

## s1-029

**Danyelle Medeiros de Araújo** (*Department of Chemistry, Universidade Federal do Rio Grande do Norte, Natal, Brazil*), Pablo Cañizares, Carlos Alberto Martínez-Huitle, Manuel Andres Rodrigo, Cristina Sáez Peroxo-aided Photo-electrolysis of Rhodamine B

**Danyelle Medeiros de Araújo** (Department of Chemistry, Universidade Federal do Rio Grande do Norte, Natal, Brazil), Pablo Cañizares, Carlos Alberto Martínez-Huitle, Manuel Andres Rodrigo Rodrigo, Cristina Sáez Photoelectrolyses of Rhodamine B in Chloride Media

## s1-031

Mariana Oliveira Medeiros (Instituto de Química, Universidade Federal do Rio Grande do Norte, Natal, Brazil), Djalma R. da Silva, Danyelle M. de Araújo, Karla C. de Freitas Araújo, Carlos Alberto Martínez-Huitle, Hamilton Varela

Understanding the production of persulfate using boron-doped diamond (BDD) electrode

## s1-032

Mariana Oliveira Medeiros (Instituto de Química, Universidade Federal do Rio Grande do Norte, Natal, Brazil), Carlos Alberto Martínez-Huitle, Camila Carvalho de Almeida, Dayanne Chianca de Moura, Maria Jucilene de Macedo Melo

Electrochemical effect of chloride on the oxygen evolution reaction and its application as alternative for treating an effluent using platinum and diamond anodes

## s1-033

Jéssica Pires de Paiva Barreto Instituto de Química, Universidade Federal do Rio Grande do Norte, Natal, Brazil), Carlos Alberto Martínez-Huitle, Djalma Ribeiro da Silva, Manuel Andres Rodrigo Rodrigo, Elisama Vieira dos Santos

Electrochemical properties of boron-doped diamond electrodes with low and high diamond content

## s1-034

**Paulo A. Raymundo-Pereira** (Departamento de Físico-Química, Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brazil), Thiago Canevari, Sergio A.S. Machado

Ultrasensitive Simultaneous Determination of Dihydroxybenzenes Isomers at Ultrathin Film Based on Hybrid Material SiO<sub>2</sub>/MWCNT Decorated with Ag Nanoparticles

**Manuel Andres Rodrigo** (Department of Chemical Engineering, Universidad de Castilla-la-Mancha, Ciudad Real, Spain), Pablo Cañizares, Salvador Cotillas, Javier Llanos, María José Martín de Vidales, Jose Fernando Pérez-Serrano, Cristina Sáez

Diamond anodes for the production of high value oxidants

## s1-036

**Ricardo Salazar** (Departamento de Química de los Materiales, Universidad de Santiago de Chile, Santiago, Chile), Nicole Contreras

Degradation of antihypertensive drugs Losartan and Hydrochlorothiazide in water by electro-oxidation with BDD. Application of method to tablets pharmaceuticals

## s1-037

Aline Maria Sales Solano (Departamento de Química, Universidade Federal do Rio Grande do Norte, Natal, Brazil), Maiara Barbosa Ferreira, Enric Brillas, Chrystiane do Nascimento Brito, Sergi Garcia Segura, Carlos Alberto Martínez-Huitle

Treatment of Synthetic Wastewater Containing Textile Dye Congo Red by Electro-Fenton, PhotoElectro-Fenton and Anodic Oxidation

## s1-038

Aline Maria Sales Solano (Departamento de Química, Universidade Federal do Rio Grande do Norte, Natal, Brazil), Maiara Barbosa Ferreira, Carlos Alberto Martínez-Huitle, José Heriberto Oliveira do Nascimento, Djalma Ribeiro da Silva

Electrochemical Oxidation as an Alternative to Remove Dyes from Textile Effluent using Pt and Carbon Electrodes

## s1-039

Elisama Santos (Institute of Chemistry, Federal University of Rio Grande do Norte, Natal, Brazil), Pablo Cañizares, Carlos Alberto Martínez-Huítle, Manuel Andres Rodrigo, Cristina Sáez

Electrochemical treatment with BDD anode of soil-washing effluent polluted with atrazine: Influence of particle size

Marta Santos (LAS, INPE, São José dos Campos, Brazil), Adriana Azevedo, Mauricio Baldan, Neidenei Ferreira

Method validations for high performance liquid chromatography and U/Vis to study intermediates compounds of phenol eletrooxidation using boron doped ultrananocrystalline diamonds films

## s1-041

Juan Arturo Squella (Organic and Physical Chemistry, University of Chile, Santiago, Chile), José Carbajo, Raúl Moscoso

Multiwalled carbon nanotube electrodes modified with encapsulated 3,5-dinitrobenzoic acid

## s1-043

Julio Urzúa (Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile), José Marco, Juan Arturo Squella, Claudia Yáñez Multiwalled Carbon Nanotubes-Glassy Carbon Electrodes for Electrochemical Study of 2,7-Dinitro-9-Fluorenone Adsorbed

## s1-044

Vanessa M. Vasconcelos (IQSC, USP, São Carlos, Brazil), Mauricio Baldan, Neidenei Ferreira, Marcos Lanza, Fernanda L. Migliorini, Juliana R. Steter Application of Boron-doped Diamond Electrode in Removal of Azo Dye Reactive Black 5

## Session 2

## Room: Brisa 2/3

#### s2-001

Antonio Angelo (Department of Chemistry, State University of São Paulo, Bauru, Brazil), Francielle Bortoloti, Amanda Garcia

The Influence of the Adsorption Sites Electronic Structure on CO Poisoning Process at Ordered Intermetallic Surfaces

#### s2-002

Abel Ibrahim Balbin Tamayo (Department of Chemistry, Pontificia Universidade Catolica do Rio de Janeiro, Rio de Janeiro, Brazil), Ana Margarita Esteva Guas, Percio Augusto Mardini Farias, Aurora Perez Gramatges A Comparative Study of Electrochemical Performance of Graphite, Modified Graphite and Graphene Oxide - Epoxy Resin Electrodes as Transducers for Biosensor Applications

#### s2-003

Abel Ibrahim Balbin Tamayo (Department of Chemistry, Pontificia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brazil), Ricardo Q. Aucêlio, Veronica Barbosa Mazza, Andrea R. da Silva, Ana Margarita Esteva Guas, Pércio Augusto Mardini Farias, Aurora Perez Gramatges Electrochemical Determination of the Diffusion Coefficient of Biological Active Naphthoquinones in Organized Medium

#### s2-004

Karina Barrezzi (Department of Chemistry, State University of São Paulo, Bauru, Brazil), Antonio Angelo, Francielle Bortoloti, Jéssica Garcia, Amanda Garcia

Ordering Effect on the Electroactivity of Noble Metals Intermetallics Toward Glycerol Eletrooxidation Reaction

#### s2-005

**Soledad Bollo** (*Bioelectrochemistry Lab., University of Chile, Santiago, Chile*), Daniela Baez, Jose Marco, Claudia Yañez, Helena Pardo, Ignacio Laborda Effect of reduction method of graphene oxide on the electrochemical response of a DNA biosensor

## s2-006

Othon S. Campos (Departamento de Química Fundamental, Universidade de São Paulo, São Paulo, Brazil), Rafael M. Buoro, Sérgio H. Domingues, A. William O. Lima, Jairo J. Pedrotti, Silvia Serrano

Simultaneous Detection of Noradrenaline, Acetaminophen, Xanthine and Theophylline at a Sensor Based on a Graphene Oxide and o-Dihydroxy Catechol Modified Glassy Carbon Electrode

## s2-007

**Camila Canales** (*Quimica Inorganica, Facultad de Quimica, Pontificia Universidad Catolica de Chile, Santiago, Chile*), Galo Ramirez

Glassy carbon electrodes modified by supramolecular assemblies of metalloporphyrins. Effect on the method of modification towards hydrogen evolution

#### s2-008

Jussara Carneiro (Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brazil), Rodnei Bertazzoli, Peter Hammer, Marcos Lanza, Jonas Reis, Mauro Santos

The catalytic activity of zirconium oxide–Printex 6L carbon composite towards oxygen reduction reaction

#### s2-009

**Jussara Carneiro** (Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brazil), Rodnei Bertazzoli, Peter Hammer, Marcos Lanza, Jonas Reis, Mauro Santos

Study of the catalytic efficiency of tantalum oxide supported on Printex 6L carbon for the electrosynthesis of hydrogen peroxide

#### s2-010

**Fernando Miguel Amorim de Lino** (*Faculty of Pharmacy, UFG, Goiania, Brazil*) Aparecido Souza, Micheli Quintino, Eric Gil, Luanne F. Garcia Copper Oxide-modified Carbon Paste Electrode on Determination of Catechol

#### s2-011

**Tayla Fernanda Serantoni da Silveira** (Física e Química, Universidade Estadual Paulista Júlio de Mesquita Filho, Ilha Solteira, Brazil), Devaney Ribeiro do Carmo

Preparation, Characterization and Application of a Novel Composite Obtained Through Zr(IV) Isopropoxide and Phosphoric Acid

Xiangyun Deng (Institute of Physics and Materials Science, Tianjin Normal University, Tianjin, China), Chen Chen, Lei Dong, Xifei Li, Dejun Li Influence of TiN Films with Different Thickness on LiFePO<sub>4</sub>/C Ca-thode Performance Using Magnetron Sputtering

### s2-013

Paula Caldevilla Collado (R&D, DropSens S.L., Llanera, Spain), David Hernández-Santos, Marta M. P. S. Neves, Pablo Fanjul Streptavidin-functionalized Ferromagnetic Nickel Nanowires: a New Tool for Bioanalytical Applications

### s2-014

**Christopher Foster** (Science and Engineering, Manchester Metropolitan University, Manchester, United Kingdom), Craig Banks

Designing electrochemically efficient screen-printed sensors: Exploring the effect of electrochemical performance on electrode distance

### s2-015

Geiser Gabriel Oliveira (Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brazil), Orlando Fatibello-Filho, Marcos Lanza, Bruna C. Lourenção, Laís S. Pereira, Fernando C. Vicentini

Evaluation of a Glassy Carbon Electrode Modified with Printex 6L Carbon Black for the Development of Electrochemical Sensors

### s2-016

Jarem Garcia (Department of Chemistry, State University of Ponta Grossa, Ponta Grossa, Brazil), Alan Ben-Hur Bischof, Sérgio Ricardo de Lazaro, Fábio Santana dos Santos, Rodolfo Bonotto Estevan, Rodolfo Thiago Ferreira, Karine Klider, Gustavo Marciniuk, Alex Vieira Pedroso, Christiana Andrade Pessoa, Karen Wohnrath

Control of the Properties of the Graphene Layers Produced from the Electrochemical Exfoliation of Low Cost Graphite Materials

### s2-017

**Roger Gonçalves** (Department of Chemistry, Universidade Federal de São Carlos, São Carlos, Brazil), Fernando C. Moraes, Ernesto Chaves Pereira

Improvement of Water Splitting Reaction Over Poly(3-hexylthiophene) Modified with Reduced Graphene Oxide

**Barbara Kowalewska** (Department of Chemistry, University of Warsan, Warsan, Poland), Katarzyna Jakubow

Direct Electrochemistry of Flavin-Dependent Oxidases Assembled on Electrochemically Reduced Graphene Oxide-Carbon Nanotubes Hybrid System for Glucose and Lactate Biosensing

#### s2-020

David Fermin (School of Chemistry, University of Bristol, Bristol, United Kingdom), Alfredo C. Peterlevitz, Paul W. May, Robert Harniman, Vitor Baranauskas, Hudson Zanin

Novel class of interconnected carbon nanospheres

#### s2-021

**Dejun Li** (Institute of Physics and Materials Science, Tianjin Normal University, Tianjin, China), Lei Dong, Jianmin Feng, Yan Han, Xifei Li Efficient Chemical Exfoliation of N-doped Graphene from Ncontaining Bamboo-like Carbon Nanotubes

#### s2-022

**Dejun Li** (Institute of Physics and Materials Science, Tianjin Normal University, Tianjin, China), Lei Dong, Jianmin Feng, Yan Han, Xifei Li, Shuangxi Liu CoO modified porous carbon anode enhancing electrochemical performance of Li-ion batteries

#### s2-023

Sergio A.S. Machado (Department of Chemistry, State São Paulo University, São Carlos, Brazil), Anderson Campos, Thiago Canevari, Fernando Cincotto Simultaneous determination of epinephrine and dopamine by electrochemical reduction on the hybrid material SiO<sub>2</sub>/graphene content Ag nanoparticles

#### s2-024

Sergio A.S. Machado (Department of Chemistry, State São Paulo University,

São Carlos, Brazil), Thiago Canevari, Fernando Cincotto, Richard Landers Synthesis and characterization of nickel (II) hydroxide particles on Silica/GO matrix and its application in a sensitive electrochemical sensor for vitamin D determination

**Wesley Machini** (Department of Physics, Chemistry and Biology, São Paulo State University, Presidente Prudente, Brazil), Marcos Teixeira

Electrochemical Properties of the Oxo-manganese-Schiff Complex and its Electrocatalytic Application as Enzymatic Biomimicking

#### s2-026

Petr Mazur (New Technologies - Research Centre, University of West Bohemia, Plzen, Czech Republic), Jan Dundalek, Romana Fojtikova, Juraj Kosek, Jaromir Pocedic

 ${\rm MnO}_2-{\rm carbon}$  nano-composites prepared by electros praying as electrodes for supercapacitors

#### s2-027

Eva Menart (Analytical Chemistry Laboratory, National Institute of Chemistry, Ljubljana, Slovenia), Samo B. Hoèevar, Vasko Jovanovski

Silver nanoparticles-decorated carbon in ionic liquid carbon paste electrode for improved determination of nitrite

#### s2-028

Fernando C. Moraes (Department of Chemistry, UFSCar, São Carlos, Brazil), Maria Donatoni, Kleber Oliveira, Bruno Rossi, Ernesto C. Pereira Electrochemical Sensor Based on Reduced Graphene Oxide Modified with Cu(II)-meso-Tetrathienyl Porphyrin for Determination of Endocrine Disruptor

#### s2-029

Laura Novais (Department of Chemistry, University of São Paulo, Ribeirão Preto, Brazil), Wesley Muscelli, Herenilton Oliveira

Voltammetric Properties of Glassy Polymeric Carbon Obtained at Different Synthesis Temperature

#### s2-030

Laura Novais (Department of Chemistry, University of São Paulo, Ribeirão Preto, Brazil), Raissa de Camargo, Herenilton Oliveira

Synthesis, and Voltammetric Properties of Fe and Co Ions Modified Glassy Polymeric Carbon

Silvia Sizuka Oishi (Laboratório Associado de Sensores e Materiais, Instituto Nacional de Pesquisas Espaciais - INPE, São Jose dos Campos, Brazil), Mauricio Baldan, Edson Cocchieri Botelho, Andrea Couto, Neidenei Ferreira, Mirabel Cerqueira Rezende

Electrochemical Reduction of Nitrate Using Boron-doped Nanocrystalline Diamond Grown on Reticulated Vitreous Carbon

#### s2-032

**Emiliano Primo** (Departamento de Fisico-química, Facultad de Cs. Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina), Soledad Bollo, Gustavo Rivas, M. Dolores Rubianes

Towards Rational Design of Gold Platforms for Protein Biosensing with Various Graphene-derived Materials

#### s2-033

**Robson Rocha** (*EESC, USP, São Carlos, Brazil*), Jussara Carneiro, Marcos Lanza, Fernando Lindo, Geiser Oliveira, Ricardo Valim, Marcelo Zaiat Study of the oxygen reduction reaction on carbon black modified with Nb-Ru binary oxides

#### s2-034

Fernando Lindo Silva (Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brazil), Matheus S. Kronka, Marcos Lanza

Study of the oxygen reduction reaction on carbon black modified with 9,10-Phenanthrenequinone

#### s2-035

Daniela Rodrigues Silvestrini (Física e Química, Universidade Estadual Paulista Júlio de Mesquita Filho, Ilha Solteira, Brazil), Urquisa de Oliveira Bicalho, Devaney Ribeiro do Carmo

Silsesquioxane Organofunctionalized with Pamam Dendrimer and Subsequent Reaction With Copper and Potassium Hexacyanoferrate (III) for Determination of Ascorbic Acid

#### s2-036

Fernanda Souza (Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brazil), Pablo Cañizares, Marcos Lanza, Manuel Andres Rodrigo, Cristina Sáez

The effect of diamond/graphite carbon compositions in electrochemical oxidation reactivity

Marcos Teixeira (Faculty of Science and Technology, São Paulo State University, Presidente Prudente, Brazil), Christopher Brett, Diego David-Parra, Carla Gouveia-Caridade, Wesley Machini

Electrochemical Impedance Spectroscopic Study of Poly(Bismarck R)

#### s2-039

Leandro Trevelin (Departamento de Química e Física Molecular, Instituto de Química de São Carlos, São Carlos, Brazil), Marcos Lanza, Robson Rocha, Ricardo Valim

Acid medium evaluation of ORR using catalysts modified with mixed oxides of Niobium and Molybdenum supported on Printex 6L carbon

#### s2-040

Vanessa M. Vasconcelos (IQSC, USP, São Carlos, Brazil), Marcos Lanza, Carlos Ponce-de-Leon

Removal of Textile Dye RB-19 using a Filter-Press Reactor with Reticulated Vitreous Carbon as Cathode

#### s2-041

**Claudia Yañez** (Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile), José Marco, Elias Villalobos

Preparation and Characterization of Cyclodextrin Modified Graphene Oxide for Molecular Recognition Mediated by Host-Guest Interaction

### s2-042

Kalle Salminen (Department of Chemistry, Aalto University, Espoo, Finland) Hot Electron-Induced Electrochemiluminescence at Carbon Electrodes

### s1-043

**Omotayo Arotiba** (*Applied Chemistry*, University of Johannesburg, Johannesburg, South Africa)

Electrochemical Application of Exfoliated Graphite-Diamond Mixed Carbon Electrodes in Water Treatment

# Index

## Α

Abbas, Qamar, (Tue s1)10:40 Abdelkareem, Mohammad, (Wed s1)11:30 Abdelmawgoud, Khalil, (Wed s1)17:50 Adekunle, Abolanle S., (Tue s2)09:20, (Wed s2)17:30 Agegnehu, Abiye Kebede, (Wed s1)10:00 Akerlund, Hans-Erik, (Wed s2)11:30 Albertsson, Per-Åke, (Wed s2)11:30 Almeida, Eduardo, s1-008 Alvarez-Lueje, Alejandro, s1-001 Alves de Lima Almeida, Dalva, s1-017 Ameida, Joseany de Moraes Santos, s1-002 Amorim de Lino, Fernando Miguel, s2-010 Amstutz, Véronique, (Tue s2)11:10 Angelo, Antonio, s2-001, s2-004 Antonio, Jadielson L., (Mon s1)16:20 Araneda, Camila, s1-013 Araujo da Costa, Vilma, s1-003 Araujo, Josimar A., s1-025 Araujo, Thaylan P., (*Tue s2*)09:40, s1-025 Armijo, Francisco, s1-013 Artyushkova, Kateryna, (Mon s1)17:30 Asai, Miyuki, s1-009 Atanassov, Plamen, (Mon s1)17:30 Athie Goulart, Lorena, s1-004 Atique Sawazaki, David Tatsuo, (Mon s2)16:00 Aucélio, Ricardo Queiroz, s1-002, s2-003 Azevedo, Adriana, s1-040

#### В

Babuchowka, Paulina, (Tue s1)10:40 Baez, Daniela, s2-005 Balbin Tamayo, Abel Ibrahim, s2-002, s2-003 Baldan, Mauricio, s1-011, s1-016, s1-040, s1-044, s2-031 Banks, Craig, (Wed s2)08:30, s2-014 Barakat, Nasser A. M., (Wed s1)11:30, (Wed s1)17:50 Baranauskas, Vitor, s2-020 Barbosa Ferreira, Maiara, s1-037, s1-038 Barbosa Mazza, Veronica, s2-003 Barrezzi, Karina, s2-004

Barros, Willyam, (Wed s1)17:30 Barsan, Madalina, (Tue s2)08:30 Barton, Jan, (Wed s1)11:50 Barzegar, Farshad, (Tue s1)09:20 Béguin, François, (Tue s1)09:40, (*Tue s1*)10:40, (*Thu s1*)09:00 Bekir Yildiz, Huseyin, (Wed s2)11:30 Bélanger, Daniel, (Wed s1)10:40 Bello, Abdulhakeem, (Tue s1)09:20 Benchirouf, Abderrahmane, (Wed s2)17:50 Benjamin, Stephen, (Wed s2)16:00 Bergamini, Marcio, s1-024 Bergren, Adam, (Mon s0)11:50 Bertazzoli, Rodnei, (Wed s1)17:30, s2-008, s2-009 Bertoncello, Paolo, (Tue s2)11:50 Biaggio, Sonia R., s1-005, s1-007, s1-012 Bicalho, Urquisa de Oliveira, s2-035 Billon, Florence, (Wed s1)09:00 Binder, Paul, (Mon s2)16:20 Bischof, Alan Ben-Hur, s2-016 Bocchi, Nerilso, s1-005, s1-007, s1-012 Bollo, Soledad, s1-019, s2-005, s2-032 Bondarenko, Alexandra, s1-010 Bortoloti, Francielle, s2-001, s2-004 Botelho, Edson Cocchieri, s2-031 Brett, Christopher, (Tue s2)08:30, s2-038 Brillas, Enric, (Thu s2)08:30, s1-037 Brocenschi, Ricardo, s1-006, s1-007 Brooksby, Paula, (Wed s1)15:30 Brousse, Thierry, (Tue s1)09:40, (Wed s1)10:40 Brown, Simon, (Wed s1)15:30 Buoro, Rafael, s1-018, s2-006 Byers, Joshua C., (Wed s1)09:00 С

Calvert, Paul, (Wed s2)11:50 Calvo, Ernesto, (Thu s2)10:40 Caldevilla Collado, Paula, s2-013 Camargo, Maiui, (Tue s2)10:40 Campos, Anderson, s2-023 Campos, Othon S., s1-018, s2-006 Canales, Camila, s2-007 Canevari, Thiago, s1-034, s2-023, s2-024 Cañizares, Pablo, (*Wed s1*)17:00, s1-029, s1-030, s1-035, s1-039, s2-036 Carbajo, José, s1-041 Cardoso, Rafael, s1-008 Carneiro, Jussara, (Wed s1)17:30, s2-008, s2-009, s2-033 Carvalho de Almeida, Camila, s1-032 Cem Emek, Sinan, (Wed s2)11:30 Cericola, Dario, (Thu s1)11:40 Cerro-Lopez, Monica, (Thu s2)09:20 Chen, Chen, s2-012 Chen, Rongzhi, s1-009 Chianca de Moura, Dayanne, s1-032 Choi, Mansoo, s2-018 Cigler, Petr, (Wed s1)11:50 Cincotto, Fernando, s2-023, s2-024 Cintra Fernandes, Neemias, (Thu s2)10:00 Colombo, Rafael N. P., (Mon s1)16:20 Contreras, Nicole, s1-036 Corat, Evaldo, s1-015 Cordoba de Torresi, Susana, (Mon s1)16:20 Correa, Daniel, s1-013 Cortés-Salazar, Fernando, (Tue s2)11:10, s1-010 Costa Bassetto, Victor, s1-010 Cotillas, Salvador, (Wed s1)17:00, s1-035 Couto, Andrea, s1-011, s2-031 Crosnier, Olivier, (Tue s1)09:40 Cuesta, Angel, (Mon s1)17:50

#### D

da Silva, Andrea R., s2-003 da Silva, Bianca F., s1-005, s1-007 da Silva, Djalma R., (Mon s2)17:00, s1-031 da Silveira, Tayla Fernanda Serantoni, s2-011 Daems, Nick, (Thu s2)11:00 Dall Antonia, Luiz Henrique, (Thu s2)09:40 Dangbegnon, Kouadio Julien, (Tue s1)09:20 David-Parra, Diego, s2-038 Davoglio, Rogério A., s1-012 de Araújo, Danyelle M., (Mon s2)17:00, s1-003, s1-031 de Camargo, Raissa, s2-030 de Freitas Araújo, Karla C., s1-031 de Lazaro, Sérgio Ricardo, s2-016 de Souza Gil, Eric, (Thu s2)10:00 de Souza, Victor Hugo R., (Tue s1)11:10 del Pozo Vazquez, Maria, (Thu s2)10:40

del Rio, Rodrigo, s1-013 Demir, Umit, (*Tue s2*)10:00 Deng, Xiangyun, s2-012 Deslouis, Claude, (Mon s1)17:00, (Wed s1)09:00 Dilgin, Yusuf, (Wed s2)11:30 Dixon, Ditty, (Thu s1)10:40 do Carmo, Devaney Ribeiro, s2-011, s2-035 do Nascimento Brito, Chrystiane, (Mon s2)17:00, s1-037 Domingues, Sérgio H., s2-006 Donatoni, Maria, s2-028 Dong, Lei, s2-012, s2-021, s2-022 Dornellas, Rafael, s1-002, s1-008 dos Santos, Fábio Santana, s2-016 Downard, Alison, (Wed s1)15:30 Dryfe, Robert, (Wed s2)09:20, (Thu s2)11:40 Dubale, Amare Aregahegn, (Wed s1)10:00 Dundalek, Jan, (Thu s1)11:00, s2-026

#### Ε

Ebenso, Eno E., (Tue s2)09:20, (Wed s2)17:30 Eguílaz, Marcos, (Wed s2)16:20 Einaga, Yasuaki, (Mon s2)15:30 El Kadib, Abdelkrim, (Thu s1)10:00 El-Deen, Ahmed G., (Wed s1)17:50 Enache, T. Adrian, (Wed s2)11:10 Escobar, Freddy, (Thu s1)10:00 Eskusson, Jaanus, (Tue s1)10:00, (Tue s1)11:50 Espinoza-Montero, Patricio Javier, s1-014 Esteva Guas, Ana Margarita, s2-002, s2-003 Estevan, Rodolfo Bonotto, s2-016 Evrard, David, (Mon s2)17:50 F

Fanjul, Pablo, s2-013 Farquhar, Anna, (Wed s1)15:30 Fatibello-Filho, Orlando, (Wed s2)17:00, s1-015, s1-020, s2-015 Fayemi, Omolola E., (Tue s2)09:20 Feng, Jianmin, s2-021, s2-022 Fereiro, Jerry, (Mon s0)11:50 Fermin, David, (Mon s1)15:30, s2-020 Ferreira Garcia, Luane, (Thu s2)10:00 Ferreira, Neidenei, s1-011, s1-040, s1-044, s2-031 Ferreira, Neidenei Gomes, s1-016, s1-017 Ferreira, Rodolfo Thiago, s2-016

Ferreryra, Nancy, (Wed s2)16:20
Fic, Krzysztof, (Tue s1)09:00, (Tue s1)09:40
Fisher, Adrian, s1-026
Fojtikova, Romana, s2-026
Foster, Christopher, s2-014
Frackowiak, Elzbieta, (Tue s1)09:00, (Thu s1)09:00
Franco, Alejandro A., (Thu s1)11:20
Freyssinier, Mathilde, (Mon s2)17:50
Frontana-Uribe, Benardo, s1-014
Fujishima, Akira, (Thu s2)11:20
Fukushima, Chikako, s1-009
Fulvio, Pasquale, (Thu s1)09:40

#### G

Gao, Fang, (Mon s0)10:10 Garcia, Amanda, s2-001, s2-004 Garcia, Jarem, s2-016 Garcia, Jéssica, s2-004 Garcia, Luane, (Wed s2)16:00 Garcia, Luanne F., s2-010 Garcia, Renato G., (Mon s1)17:50 Garcia Segura, Sergi, s1-037 Garcia-Garcia, Alejandra, (Thu s2)09:20 Gasnier, Aurelien, (Wed s2)16:20 Ghica, Mariana Emilia, (Tue s2)08:30 Gil, Eric, (Wed s2)16:00, s2-010 Girault, Hubert H., (Tue s2)11:10, s1-010 Golveia, Jhéssica, (Wed s2)16:00 Gomes, Caroline, s1-018 Gómez-Cámer, Juan Luis, (Thu s1)11:40 Gonçales, Vinicius R., (Mon s1)16:20 Gonçalves, Roger, s2-017 Gorton, Lo, (Wed s2)11:30 Goubaa, Hamza, (Thu s1)10:00 Gouveia-Caridade, Carla, (Tue s2)08:30, s2-038 Groenen-Serrano, Karine, (Mon s2)17:50 Gros, Pierre, (Mon s2)17:50 Grützke, Martin, (Tue s1)11:30 Gu, Yunfeng, s1-026 Guery, Claude, (Thu s1)11:20 Guldi, Dirk, (Wed s1)08:30 Gutiérrez, Alejandro, (Wed s2)16:20 Gutiérrez, Cristian, (Mon s1)16:00 Gutierrez, Fabiana Andrea, (Wed s2)16:20, s1-019

#### Н

Hägerhäll, Cecilia, (Wed s2)11:30 Härk, Eneli, (Wed s1)11:10, (Thu s1)09:20 Hammer, Peter, s2-008, s2-009 Han, Yan, s2-021, s2-022 Hapiot, Philippe, (Wed s1)15:30 Harniman, Robert, s2-020 Hassan, Kamrul, (Wed s2)11:30 Hayashi, Mio, (Thu s2)11:20 Hernández-Santos, David, s2-013 Herrasti, Pilar, s1-019 Herrera, Santiago, (Thu s2)10:40 Hirono, Shigeru, (Wed s2)15:30 Hirota, Kazuo, (Thu s2)11:20 Hoèevar, Samo B., (Tue s2)11:30, s2-027 Hubin, Annick, (Thu s2)11:00 Hucke, Thomas, (Thu s1)11:40 Hurt, Robert, (Mon s0)08:40 Husmann, Samantha, (Wed s2)09:40 Hwang, Bing-Joe, (Wed s1)10:00, (Thu s1)08:30

#### I

Ibanez, Jorge G., s1-014 Irikura, Kallyni, s1-006, s1-020 Isaïe Maye, Sunny, s1-010

#### J

Jäger, Rutha, (*Wed s1*)11:10, (*Thu s1*)09:20 Jänes, Alar, (*Tue s1*)10:00, (*Tue s1*)11:50 Jakubow, Katarzyna, s1-021, s1-022, s2-019 Jara-Ulloa, Paola, s1-023 Jarosova, Romana, (*Wed s2*)10:40 Jezowski, Pawel, (*Tue s1*)09:40 Jones, Thomas, (*Tue s2*)11:50 Jouikov, Viatcheslav, (*Wed s1*)16:00 Jovanovski, Vasko, (*Tue s2*)11:30, s2-027 Jucilene de Macedo Melo, Maria, s1-032

#### Κ

Kamata, Tomoyuki, (Wed s2)15:30 Kanarbik, Rait, (Tue s1)11:50 Kanoun, Olfa, (Wed s2)17:50 Kaspar, Robert, (Tue s2)11:50 Kato, Dai, (Wed s2)15:30 Kavan, Ladislav, (Wed s1)11:50 Kavanagh, Paul, (Wed s1)09:40 Kawamoto, Tohru, s1-009 Khalil, Khalil, (Wed s1)11:30 Kim, Hyun-Soo, s2-018

Klider, Karine, s2-016 Kondo, Takeshi, (Thu s2)11:20 Kosek, Juraj, (Thu s1)11:00, s2-026 Kovaè, Janez, (Tue s2)11:30 Kowalewska, Barbara, (Tue s2)09:00, s1-021, s1-022, s2-019 Kronka, Matheus S., s2-034 Krysova, Hana, (Wed s1)11:50 Kubota, Lauro, (Tue s2)10:40 Kumar, Rakesh, (Wed s1)09:40 Kunitake, Masashi, (Wed s2)15:30 Kuraya, Eisuke, (Wed s2)15:30 Kurig, Heisi, (Tue s1)11:50 L Lahcini, Mohammed, (Thu s1)10:00 Laheäär, Ann, (Tue s1)11:50 Landers, Richard, s2-024 Lanza, Marcos, (Wed s1)17:30, s1-016, s1-044, s2-008, s2-009, s2-015, s2-033, s2-034, s2-036, s2-037, s2-039, s2-040 Le Comte, Annaïg, (Wed s1)10:40 Leão Neto, Vanildo Souza, (Thu s2)09:40 Lee, Jyh-Fu, (Wed s1)10:00 Lee, Lita, (Wed s1)15:30 Leech, Dónal, (Wed s1)09:40, (Wed s2)11:30 Leroux, Yann, (Wed s1)15:30 Lesch, Andreas, (*Tue s2*)11:10, s1-010 Letterio, Michael, (Tue s2)11:50 Lewes-Malandrakis, Georgia, (Mon s0)10:10 Li, Dejun, s2-012, s2-021, s2-022 Li, Xiang, (Thu s2)09:00 Li, Xifei, s2-012, s2-021, s2-022 Lima, A. William O., s2-006 Lin, Zhirong, (Mon s2)17:30 Lindo, Fernando, s2-033 Lisboa, Fabio S., s1-024 Liu, Shuangxi, s2-022 Llanos, Javier, (Wed s1)17:00, s1-035 Lodovico, Lucas, (Wed s2)09:00 Lopes, Flavio, (Wed s2)16:00 Lopes, Ilanna C., (Tue s2)09:40, s1-025 Lourenção, Bruna C., s2-015 Lucas, Ivan T., (Thu s1)10:00 Luque, Guillermina, (Wed s2)16:20 Lust, Enn, (Tue s1)10:00, (Tue s1)11:50, (Wed s1)11:10, (Thu s1)09:20

#### Μ

Ma, Haifeng, (Wed s1)15:30 Ma, Hongkai, s1-026 Mac Kenna, Nicky, (Wed s2)11:50 Machado Dornellas, Rafael, s1-027 Machado, Sergio A.S., s1-034, s2-023, s2-024 Machini, Wesley, s2-025, s2-038 Manyala, Ncholu, (Tue s1)09:20 Marchini, Florencia, (Thu s2)10:40 Marciniuk, Gustavo, s2-016 Marco, José, s1-043, s2-005, s2-041 Marcolino Jr, Luiz Humberto, (Wed s1)16:20, s1-024 Mardini Farias, Pércio Augusto, s2-003 Maroneze, Camila, (Tue s2)10:40 Martín de Vidales, María José, (Wed s1)17:00, s1-035 Martínez-Huitle, Carlos Alberto, (Mon s2)17:00, s1-003, s1-029, s1-030, s1-031, s1-032, s1-033, s1-037, s1-038, s1-039 Mascaro, Lucia, s1-004, s1-028 Matsubara, Elaine Y., (Mon s1)16:20 Mauleon Amieva, Abraham, (Thu s2)09:20 May, Paul, (Mon s1)15:30, s1-015, s2-020 Mayara, Camila Duarte de Oliveira, s1-017 Mazario, Eva, s1-019 Mazur, Petr, (Thu s1)11:00, s2-026 McCreery, Richard, (Mon s0)11:50 Meas-Vong, Yunny, (Thu s2)09:20 Medeiros de Araújo, Danyelle, s1-029, s1-030 Meller, Mikolaj, (Tue s1)09:00 Menart, Eva, (Tue s2)11:30, s2-027 Migliorini, Fernanda, s1-011, s1-016, s1-044 Miguel de Amorim Lino, Fernando, (Thu s2)10:00 Millet, Pierre, (Wed s2)10:00 Minadeo, Marco A. de O., (Mon s1)16:20 Mochalin, Vadym, (Tue s1)08:30 Möller, Priit, (Tue s1)11:50 Momodu, Damilola, (Tue s1)09:20 Moncada, Viviana, s1-001 Montes, Rodrigo, s1-008 Moraes, Fernando C., (Mon s1)17:50, s2-017, s2-028 Morcrette, Mathieu, (Thu s1)11:20 Morrin, Aoife, (Wed s2)11:50

Moscoso, Raúl, s1-041 Motlak, Moaaed, (Wed s1)11:30 Moulton, Simon E., (Wed s2)11:50 Mozhzhukhina, Nataliia, (Thu s2)10:40 Mphuthi, Ntsoaki, (Wed s2)17:30 Müller, Christian, (Wed s2)17:50 Müller-Sebert, Wolfgang, (Mon s0)10:10 Munoz, Rodrigo, s1-008 Muñoz, Rodrigo Alejandro Abarza, s1-027 Munson, Catherine, (Wed s2)10:40 Muscelli, Wesley, s2-029

#### Ν

Naal, Zeki, (Mon s2)16:00 Nagaiah, Tharamani C., (Wed s1)09:20 Nebel, Christoph, (Mon s0)10:10 Neiva, Eduardo G. C., (Wed s1)16:20 Nesladek, Milos, (Wed s1)11:50 Neves, Marta M. P. S., s2-013 Niwa, Osamu, (Wed s2)15:30 Nossol, Edson, s1-008 Notargiacomo, Andrea, (Tue s2)11:50 Novais, Laura, s2-029, s2-030 Novák, Petr, (Thu s1)11:40 Nowak, Sascha, (Tue s1)11:30

#### 0

O'Conghaile, Peter, (Wed s1)09:40, (Wed s2)11:30 Ochiai, Tsuyoshi, (Thu s2)11:20 Ogorevc, Bozidar, (Tue s2)11:30 Oishi, Silvia Sizuka, s2-031 Oliveira do Nascimento, José Heriberto, s1-038 Oliveira, Geiser, (Wed s1)17:30, s2-015, s2-033 Oliveira, Herenilton, s2-029, s2-030 Oliveira, Kleber, s2-028 Oliveira, Marcela M., (Tue s1)11:10 Oliveira Medeiros, Mariana, s1-031, s1-032 Oliveira, Regina V., s1-005 Oliveira, S. Carlos B., (Wed s2)11:10 Oliveira-Brett, Ana Maria, (Wed s2)11:10 Osadebe, Isioma, (Wed s1)09:40 Oznülüer, Tuba, (Tue s2)10:00 Oztürk Doğan, Hülya, (Tue s2)10:00

#### Ρ

Packer, Michael A., (Wed s2)11:30 Pailleret, Alain, (Wed s1)09:00 Palm, Rasmus, (Tue s1)11:50 Pan, Chun-Jern, (Wed s1)10:00 Patyna, Adrian, (Tue s2)09:00 Pea, Marialilia, (Tue s2)11:50 Pedano, María, (Wed s2)16:20 Pedroso, Alex Vieira, s2-016 Pedrotti, Jairo J., s2-006 Pereira, Ernesto Chaves, (Mon s1)17:50, s2-017 Pereira, Gabriel F., s1-005 Pereira, Laís S., s2-015 Pérez, Bárbara, s1-001 Perez Gramatges, Aurora, s2-002, s2-003 Pérez-Serrano, Jose Fernando, (Wed s1)17:00, s1-035 Pergher, Sibele B. C., s1-003 Perrot, Hubert, (Thu s1)10:00 Pescarmona, Paolo, (Thu s2)11:00 Pessoa, Christiana Andrade, s2-016 Peterlevitz, Alfredo C., s2-020 Petrak, Vaclav, (Wed s1)11:50 Pires de Paiva Barreto, Jéssica, s1-033 Pizarro, Patricia, s1-001 Pocedic, Jaromir, (Thu s1)11:00, s2-026 Pokorny, Peter, (Mon s2)16:20 Polo Fonseca, Carla, s1-017 Ponce-de-Leon, Carlos, s2-040 Poux, Tiphaine, (Thu s1)11:40 Primo, Emiliano, (Wed s2)16:20, s2-032 Pujol, Luca, (Mon s2)17:50 Puzzovio, Delia, (Tue s2)11:50

#### Q

Queiroz Aucélio, Ricardo, s1-027 Quintino, Micheli, s2-010 Quiroz, Marco A., (*Thu s2*)09:20

#### R

Rabbow, Thomas, (Mon s2)16:20
Ragupathy, Anuradha, (Wed s2)10:00
Raihane, Mustapha, (Thu s1)10:00
Raimundo de Oliveira Neto, Jerônimo, (Thu s2)10:00
Ramirez, Galo, s2-007
Ranjbari, Alireza, (Wed s2)10:00
Ratajczak, Paula, (Tue s1)10:40
Raymundo-Pereira, Paulo A., s1-034
Recio, F. Javier, (Mon s1)16:00, s1-019
Reis, Jonas, (Wed s1)17:30, s2-008, s2-009
Ressam, Ibtissam, (Thu s1)10:00
Rezende, Mirabel Cerqueira, s2-031

Ribeiro Baldan, Maurício, s1-017 Ribeiro da Silva, Djalma, s1-033, s1-038 Richter, Eduardo, s1-008 Rivas, Gustavo, (Wed s2)16:20, s1-019, s2-032 Rocha, Robson, (Wed s1)17:30, s2-033, s2-039 Rocha-Filho, Romeu C., s1-005, s1-006, s1-007, s1-012, s1-020 Rodgers, Andrew, (Thu s2)11:40 Rodrigo, Manuel Andres, (Mon s2)17:00, (Wed s1)17:00, s1-029, s1-035, s1-039, s2-036 Rodrigo Rodrigo, Manuel Andres, s1-030, s1-033 Rodrigues, Adriana P., (Tue s2)09:40 Rodríguez, Marcela, (Wed s2)16:20 Romann, Tavo, (Wed s1)11:10 Rosolen, José Maurício, (Mon s1)16:20, (Wed s2)09:00 Rossi, Bruno, s2-028 Rothermel, Sergej, (Tue s1)11:30 Rubianes, María, (Wed s2)16:20, s1-019, s2-032 Rubio, Maria Jose, s1-013 Ruffien-Ciszak, Audrey, (Mon s2)17:50 Ruoff, Rodney, (Mon s0)09:30

#### S

Sáez, Cristina, (Wed s1)17:00, s1-029, s1-030, s1-035, s1-039, s2-036 Salazar, Ricardo, s1-036 Sales Solano, Aline Maria, s1-037, s1-038 Sanli, Abdulkadir, (Wed s2)17:50 Santhiago, Murilo, (Tue s2)10:40 Santiago, Mariangela, (Wed s2)16:00 Santos, Elisama, s1-039 Santos, Marta, s1-040 Santos, Mauro, (Wed s1)17:30, s2-008, s2-009 Satomura, Kazuhito, (Thu s2)11:20 Sayed, Sayed, (Mon s0)11:50 Scontri, Mateus, s1-042 Sel, Ozlem, (*Thu s1*)10:00 Semenikhin, Oleg A., (Wed s1)09:00 Serov, Alexey, (Mon s1)17:30 Serrano, Silvia, s1-018, s2-006 Silva, Cecilia, (Tue s2)10:40 Silva, Fernando, (Wed s1)17:30

Silva, Fernando Lindo, s2-034 Silva, Iranaldo S., s1-025 Silva, Tiago, s1-015 Silvestrini, Daniela Rodrigues, s2-035 Simonet, Jacques, (Wed s1)16:00 Skowron, Piotr, (Thu s1)09:00 Souza, Aparecido, s2-010 Souza, Fernanda, s2-036 Spahr, Michael E., (Thu s1)11:40 Sperling, Eva, (Wed s2)11:30 Squella, Juan Arturo, s1-041, s1-043 Steegstra, Patrick, (Thu s2)11:00 Steter, Juliana R., s1-044 Su, Wei-Nien, (Wed s1)10:00 Suzuki, Edgar, (Mon s2)16:00 Swain, Greg, (Wed s2)10:40, s1-020 Szeto, Bryan, (Mon s0)11:50

#### Т

Tacchini, Philippe, (Tue s2)11:10 Taghizadeh, Fatemeh, (Tue s1)09:20 Tago, Shoko, (Thu s2)11:20 Tallo, Indrek, (Tue s1)11:50 Tamirat, Andebet Gedamu, (Wed s1)10:00 Tanaka, Auro A., (Tue s2)09:40, s1-025 Tanaka, Hisashi, s1-009 Tanaka, Sonia Maria C. N., (Tue s2)09:40, s1-025 Tasca, Federico, (Mon s1)16:00 Tee, Ester, (*Tue s1*)11:50 Teixeira, Marcos, s2-025, s2-038 Tesio, Alvaro, (Thu s2)10:40 Thakur, Abhimanyu Das, (Wed s2)17:50 Thomberg, Thomas, (Tue s1)10:00 Torres, Walter, (Thu s2)10:40 Torresi, Roberto, (Wed s2)09:00 Trampert, Markus, (Mon s2)16:20 Trevelin, Leandro, (Wed s1)17:30, s2-039

#### U

Urzúa, Julio, s1-043

#### V

Valim, Ricardo, (*Wed s1*)17:30, s2-033, s2-039 Vankelecom, Ivo, (*Thu s2*)11:00 Varela, Hamilton, s1-031 Vasconcelos, Vanessa M., s1-044, s2-040 Vasquez-Medrano, Ruben, s1-014 Velicky, Matej, (*Wed s2*)09:20 Venegas, Ricardo, (Mon s1)16:00 Vicentini, Fernando C., s2-015 Vieira dos Santos, Elisama, s1-033 Viera, Marco, (Mon s1)16:00 Villagra, Angel, (Wed s2)10:00 Villalobos, Elias, s2-041 Vlckova-Zivcova, Zuzana, (Wed s1)11:50 Vrana, Jiri, (Thu s1)11:00

#### W

Wächter, Naihara, s1-006 Wallace, Gordon G., (*Wed s2*)11:50 Wang, Yu Jue, (*Thu s2*)09:00 Watanabe, Takeshi, (*Mon s2*)15:30 Whitehead, Adam, (*Mon s2*)16:20 Williams, Federico, (*Thu s2*)10:40 Winter, Martin, (*Tue s1*)11:30 Wohnrath, Karen, s2-016 Wong, Ademar, s1-042, s2-037

#### Х

Xue, Kan-Hao, (Thu s1)11:20

#### Υ

Yan, Yushan, (*Tue s2*)11:50 Yañez, Claudia, s2-005, s2-041, s1-043 Yoshiko Matsubara, Elaine, (*Wed s2*)09:00 Yu, Gang, (*Thu s2*)09:00

#### Ζ

Zagal, Jose H., (Mon s1)16:00, s1-019 Zaiat, Marcelo, (Wed s1)17:30, s2-033 Zanin, Hudson, (Mon s1)15:30, s1-015, s2-020 Zarbin, Aldo J. G., (Tue s1)11:10, (Wed s2)09:40, (Wed s1)16:20, s1-024 Zhang, Yuanxun, s1-009

Zúñiga, César, (Mon s1)16:00

# Carbon Electrodes for Molecular Electronics

<u>Richard McCreery</u>, Adam Bergren, Jerry Fereiro, Sayed Y. Sayed, Bryan Szeto National Institute for Nanotechnology, University of Alberta 11421 Saskatchewan Drive, Edmonton, Alberta, T6G 2M9, Canada mccreery@ualberta.ca

The rapidly emerging field of Molecular Electronics investigates the behavior of organic molecules as active components in solid state electronic circuits. The focus of our research is the "molecular junction" in which a layer of molecules is oriented between two conductors, and electron transport occurs through the molecular layer. Electron transport across 1-20 nm differs fundamentally from that in standard semiconductors and thicker organic films, and often involves quantum mechanical tunneling. When molecular orbitals have suitable energies, field ionization can generate charge carriers, and transport may occur across distances much too long for tunneling. Ultraviolet photoelectron spectroscopy and photocurrent measurements from illuminated molecular junctions permit direct determination of energy levels in molecular junctions, often simultaneously with electronic conduction. A potential commercial application of molecular junctions in audio processing will also be described.



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# Modern Approaches to the Atomic-Level Design of Functional Carbon Materials

<u>Robert H. Hurt</u> Brown University Providence, Rhode Island, USA Robert Hurt@brown.edu

Carbon materials are enabling components in many current and emerging electrochemical technologies including batteries, capacitors, fuel cells, and sensors. Carbons offer an attractive set of properties for these applications that can include electrical conductivity, low chemical reactivity, dissolution and corrosion stability, high surface area, flexibility, and biocompatibility. Carbon materials have also enjoyed a special status in the general science community over the last 30 years through discoveries that have lead to two Nobel Prizes and two Kavli Prizes for nanoscience. New carbon nanoforms (fullerenes, nanotubes, graphene) have played a central role in the nanotechnology movement, where they served as models of atomic perfection that inspired the discovery and development of other 0D, 1D, and 2D materials. Thirty years of research in nanoscience has given us a portfolio of new carbon nanoforms that now serve as building blocks for the development of improved electrochemical devices.

Carbon materials do not fit readily into traditional material categories as metals, ceramics, or polymers, but have features that draw from each of the categories. Designing new carbon materials for electrochemical technologies thus requires consideration of their unique structure and properties. This talk will give an introduction to carbon materials, briefly covering their history, structure, properties, synthesis and processing methods, and electrochemical behaviors. Emphasis will be given to fundamental properties, and to the new forms that are the basis for most modern electrochemical developments. The talk will start with graphite and glassy carbon that have a long history as electrode components, and proceed to cover engineered porous carbons, diamond materials, nanotubes, and graphene. While the graphene layer has long been recognized as the basic building block of all sp<sup>2</sup>-based carbons, the isolation of the single layer in 2004 opened the scientific field of 2D materials, and has given carbon technologists a new ultrathin giant molecular building block for creation of functional 3D carbon structures. This talk will discuss the classification and nomenclature of emerging 2D carbons and review methods for assembling graphene building blocks into functional 3D electrodes.

Finally, each of the basic carbon forms can be used to fabricate hybrid materials through atomic-level doping or through the controlled co-assembly of heterostructures. Doping with nitrogen, sulfur, boron, or other heteroatoms alters electronic properties and creates new types of catalytic or electro-catalytic active sites. Carbons are often hybridized into heterostructures as supports or conductive additives, but in this role may also interact in complex and important ways with active particles modulate function. Both doping and hybridization are powerful tools now being used to add functionality to materials that consist primarily (but no longer exclusively) of carbon. The prospects for further development in the atomic-level design of functional carbon materials will be discussed.

# Thin, transparent, and conductive films of nanocomposites based on carbon nanotubes and graphene

#### Aldo J. G. Zarbin

Department of Chemistry, Federal University of Paraná (UFPR), Curitiba - PR, Brazil aldozarbin@ufpr.br

Materials deposited over different kinds of substrates as thin films represent a key-factor for several important technological applications. However, in which concerns carbon nanotubes- or graphene-based thin films, the known deposition techniques fail in at least one important requirement for good-quality films, due the lack of solubility, fusibility and processability of these nanomaterials. This restriction becomes more pronounced for carbon nanotubes- or graphene-based nanocomposites thin films, in which the carbon nanostructures are mixed with some other material, in order to take advantage of some synergistic property. Our research group has developed a very suitable route to prepare thin, transparent, and conductive films of carbon nanotubes, graphene, and their nanocomposites, stabilized at liquid-liquid interfaces. We have shown that under adequate conditions, liquid interfaces are excellent environments to stabilize thin films of unprocessable materials, which can be easily removed to any kind of ordinary substrates, including plastics. Also, chemical reactions at liquid interfaces can lead to sophisticated structures and advanced thin film materials.

The most recent results obtained in this field will be presented in this talk. The preparation, characterization, study of properties, and application in different devices of advanced materials directly obtained as self-assembled films at liquid-liquid interfaces will be discussed. Due to the particular method of preparation, the films are highly transparent, and characteristics as thickness, roughness, transparence, and conductivity can be easily controlled. The strategies and synthetic approach to prepare thin, transparent, homogeneous, and conducting films of carbon nanotubes (single or multi-walled), graphene or graphene oxide, as well as nanocomposites between these carbon nanostructures and Prussian blue, polyaniline and polythiophene will also be discussed in this talk. At the same time, a novel chemical route to graphene, starting from benzene, will be presented. Finally, the application of these films as i) ITO substitutes for transparent electrodes; ii) both transparent electrodes and active layer in photovoltaic devices; iii) electrochemical and gas sensors; iv) electrochromic materials, and v) supercapacitors will be presented and discussed in light of the structure and morphology of the nanostructured films.

# Review of the Growth and Electrochemical Properties of Carbon Nanotubes and Related Hybrid Nanostructures

<u>Jeffrey T. Glass</u><sup>a</sup>, Charles Parker<sup>a</sup>, Stephen Ubnoske<sup>b</sup>, Akshay Raut<sup>a</sup>, Billyde Brown<sup>a</sup>, Philémon A. Henry<sup>a</sup>, Brian R. Stoner<sup>a,c</sup>

<sup>a</sup>Department of Electrical and Computer Engineering and <sup>b</sup>Department of Mechanical Engineering and Materials Science, Pratt School of Engineering, Duke University, Durham, North Carolina 27708 <sup>c</sup>RTI International, Discovery-Science-Technology Division, Durham, North Carolina 27709 *email: jeff.glass@duke.edu* 

Carbon nanotubes (CNTs) have a wide array of properties that make them exciting candidates for electrodes. The geometric and chemical variations found in CNTs provide rich areas of study for both science and applications. These variations are created by the unique bonding configurations of carbon that also make it a ubiquitous part of our environment. The one dimensional nature of the basic CNT structure enables ultra-high surface area and the relative ease of attaching chemical groups to the surface provides flexible chemical functionality. This presentation will focus on multi-walled CNTs (MWCNTs) for electrochemical applications. MWCNTs are typically defined as concentric cylindrical structures with a hollow central core and can involve either a stacked cone, bamboo cross section or a hollow cylindrical core. Two primary approaches for the deposition of CNTs are: i) bulk synthesis (e.g., arc discharge or laser ablation), and ii) substrate or template synthesis (e.g., plasma enhanced chemical vapor deposition (PECVD)). Bulk synthesis enables larger quantities of materials to be produced, refined (e.g., removal of metal particles and amorphous carbon) and then later patterned or incorporated into devices. Substrate growth allows the CNTs to be deposited directly onto device substrates.

The pros and cons of various growth techniques depend on the specific application and how the CNTs will be integrated into devices. Most deposition techniques require a catalyst to facilitate decomposition of hydrocarbons and provide a dissolution host for the carbon during CNT formation. The catalyst properties and morphology impact the final CNT morphology. There is need to control both the microstructure and nanostructure of the CNT film for specific applications. Vertically aligned multi-walled carbon nanotubes (MWCNTs) have been studied to determine the electrochemical charge storage properties as a function of CNT diameter and spacing. Trends in specific capacitance can be observed that depend on the pore size regime of interest, providing an understanding of electrochemical behavior of MWCNTs over a wide range of pore sizes. Post deposition treatments of MWCNTs are also used to affect electrochemical behavior. For example, oxidation provides different electrochemical responses depending on the treatment temperature and the CNT morphology. Phenomenological models of such treatments will be discussed which explain the temperature-dependent electrochemical behavior.

An important variant of the standard nanotube can be found by integrating the CNT structure with edge structures and nanoparticles. For example, graphene edges are expected to be more reactive, hold a higher charge density and concentrate electric fields while the CNT framework can enable ultra-high surface area. Graphenated carbon nanotubes (g-CNTs) are one way to achieve this hybrid structure. This enables an optimization of charge and reactivity per unit volume not previously possible at the nanoscale. It is an engineered network with the concentration of high charge density, high reactivity edges arranged in three dimensional nanoscale space. Enhanced surface area, charge density and reactivity are expected to improve performance for a variety of applications, including; energy storage (e.g., batteries, supercapacitors), energy conversion (e.g., fuel cells), electrochemical sensors, electrodes for neural stimulation, field emission sources and electrodes for industrial processes (e.g., materials synthesis, purification). Similarly, one-dimensional nanostructures, such as oxide or metal nanoparticles, can be integrated with CNTs to provide enhanced functionality for many of these same applications. These decorated CNTs can be fabricated using post deposition processing or during growth. Many fundamental issues of CNT growth translate to the growth of integrated graphene-CNT or nanoparticle-CNT composites.

This presentation will cover the broad area of conventional CNT growth and properties as well as the formation and characterization of hybrid nanostructures, such as g-CNTs. It will also attempt to put these structures in context for electrochemical applications by examining a classification scheme based on the edge density of the nanostructures.

# Diamond for electrochemical applications: from electrode arrays to diamond foam

<u>C.E. Nebel</u>, Fang Gao, G. Lewes-Malandrakis, W. Müller-Sebert Fraunhofer-Institute for Applied Solid State Physics Tullastrasse 72, 79108 Freiburg, Germany christoph.nebel@iaf.fraunhofer.de

Electrochemical applications of materials are challenging as these devices need to work in aggressive media ranging from acids to ionic liquids to physiologic buffer solutions. Most of established substrates do not possess long term chemical stability, giving rise to decomposition, poisoning and surface fouling. In addition, future technologies will require integration into electrochemical platforms like super-caps, bio-sensors, fuel cells and water-splitting devices for energy storage and conversion, for sensing and for catalytical material processing.

In this presentation we will introduce diamond which can become a promising candidate for a variety of electrochemical application [1-3. Diamond shows superior properties for use in applications as indicated above. Diamond can be grown on large area in poly- or nano-crystalline form, either insulating (transparent) or metallically conductive using boron as p-type dopant. Diamond electrochemical surfaces can be flat and smooth; however, by top down etching or bottom up growth, we have introduced diamond wires and foam for surface enlargements in super-caps or membranes in bio-fuel cells. The surface of diamond can be terminated with a variety of atoms or molecules to control the wetting properties (hydrophobic, hydrophilic) and to tune the electron affinity with respect to electrochemical potentials. In addition, hydrogen has been shown to terminate the surface carbon bonds close to perfect which results in an unpinned surface Fermi level which can align with the chemical potential of buffer solutions. The electrochemical potential-window of diamond is significantly larger and the background current within this regime considerably lower than conventional materials. Diamond is known to be biocompatible and has therefore a potential for "in-vitro and in-vivo" electronic applications. During recent years a variety of surface modifications have been introduced and surfaces have been functionalized with DNA, enzymes and proteins. It has been demonstrated that the bonding of bio-molecules to diamond is chemically more stable than to other substrates.

In this presentation we will introduce and discuss these properties, the realization of nano-textures, nanowires and foam using self-organized particle-formation as templates for etching or overgrowth. We will show applications of diamond in ultra-micro- and nano-electrode arrays, in scanning electrochemical microscopy tips (SECM) and in super-caps as surface enlarged electrode. We will show that diamond surfaces can be hydrogen terminated to realize fast electron exchange rates using an electrochemical schema.

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#### Electronic and Morphologic Changes in Graphene Oxide upon Electrochemical Reduction

Fernando C. Moraes<sup>a</sup>, Renato G. Freitas<sup>a</sup>, Angel Cuesta<sup>b</sup> and Ernesto C. Pereira<sup>a</sup> <sup>a</sup> Departamento de Química, Universidade Federal de São Carlos São Carlos, SP, Brazil <sup>b</sup> Department of Chemistry, University of Aberdeen, Aberdeen, UK *fcmoraes@hotmail.com* 

The electronic, electrocatalytic activities and structural of graphene make it a promising material for several electrochemical devices. Reduced graphene oxide (RGO) presents an improvement of the electrical characteristics compared with the graphene oxide (GO). However, the use electrochemical method to reduce GO promotes more efficient removal of the oxygen functional groups bonded over GO surface, and creates changes on the GO morphology. These aspects results in smaller charge transfer resistance, an increase the electroactive surface area and an increase electronic conduction of the electrochemically reduced graphene oxide (ERGO). Here we report a systematic study of the changes of the ERGO surface which includes besides those properties described above changes in the morphology due to the electrochemical reduction procedure. A systematic study of the electrochemical reduction of GO was performed. GO, synthesized by the modified Hummer's method, was reduced electrochemically in phosphate buffer (pH 7.0) by applying a constant potential of -0.8 V (vs. Ag/AgCl) for different times. GO and the ERGO were characterized using ex-situ field-emission gun scanning electron microscopy (FEG-SEM), in-situ Raman scattering and in-situ atomic force microscopy (AFM). Raman scattering showed that the reduction process is accompanied by an increase in the ratio between the D and the G bands of graphene  $(I_D/I_G)$ . Electrochemical impedance spectroscopy (EIS) experiments in H<sub>2</sub>SO<sub>4</sub> containing K<sub>3</sub>[Fe(CN)<sub>6</sub>] showed that reduction of GO during 30 min promotes a decrease of the charge transfer resistance, an increase of the double-layer capacitance, and a decrease of the exponent parameter of the constant phase element ( $\alpha$ ). The decrease in the charge transfer resistance upon electrochemical reduction of GO was in agreement with the changes observed using cyclic voltammetry, which showed a reduction in the separation between  $\Delta E_{peak}$  (65 mV) as well as an increase of the current at the peaks. These results indicate that potentiostatically produced ERGO is a material suitable for electrochemical systems. FEG-SEM and AFM revealed that the reduction procedure promotes changes in the morphology of the GO sheets that lead to an increase of the system (RMS) roughness.

# Flexible and all-solid supercapacitor based on carbon nanotubes/polyaniline nanocomposite films

Victor Hugo R. de Souza\*, Marcela M. Oliveira\*\*, Aldo J. G. Zarbin\*

\*Departamento de Química, Universidade Federal do Paraná (UFPR) R. Cel. Francisco Heráclito dos Santos, 210, Jardim das Américas, 81531-970, Curitiba - PR, Brazil \*\*Departamento Acadêmico de Química e Biologia, Universidade Tecnológica Federal do Paraná (UTFPR), Curitiba-PR, Brazil

souzavhr@gmail.com

The claim in develop new materials for application in energy storage devices (supercapacitors) has growing in the last years, always combining high values of specific capacitance with the possibility to build devices lightweight and flexible. Among the several materials capable to be applied as supercapacitors, single wall carbon nanotubes (SWNT) and polyaniline (PAni) nanocomposites are very promising, since these ones combine the desirable properties of the SWNT, as the high electron conductivity[1], with the tunable properties of the conducting polymer, as the easy doping/undoping process responsible by the pseudocapacitive behavior[2]. We developed a novel route for prepare freestanding interfacial thin films, based on a two immiscible liquids, and it has shown to be a interesting way for carbon materials/polyaniline nanocomposites, resulting in materials capable to be deposited over different substrates[3-4].

Herein, an all-solid supercapacitor was prepared from a SWNT/PAni nanocomposite synthesized from the interfacial polymerization of the aniline [5]. Afterwards, the material was deposited over a flexible substrate (polyethylene terephthalate-PET) which was previously covered with a chromium/gold mask for electrical contact. A polyvinyl alcohol (PVA)/H<sub>2</sub>SO<sub>4</sub> 1 mol.L<sup>-1</sup> gel electrolyte was used as solid separator. The schematic representation of the device can be seen in the Figure 1 (left). The all-solid device presented a good value of volumetric specific capacitance (76.7 F.cm<sup>-3</sup>), besides presenting a high charge/discharge stability (around 90%) after 1000 cycles. The all-solid capacitor also showed the pseudocapacitive behavior even when submitted to mechanical deformation (100 twisting process-Figure 1 (right)), opening the possibility for further application in flexible devices. A low charge transfer resistance value (23 Ohm) was detected through the electrochemical impedance spectroscopy (EIS) indicating a good electron conductivity and good faradaic reversibility of the all solid device.

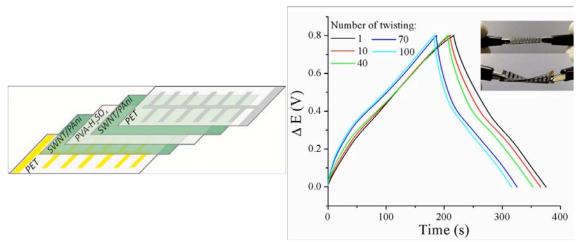


Figure 1 - (Left) Schematic representation of the device and (right) charge-discharge behavior after several deformations.

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# Synthesis and Characterization of Graphene/Ni(OH)<sub>2</sub> Nanocomposites Obtained by Polyol Method and Electrochemical Characterization in Alkaline Medium

Eduardo G. C. Neiva, Luiz H. Marcolino Jr., Aldo J. G. Zarbin <sup>1</sup>Department of Chemistry, Universidade Federal do Paraná (UFPR) Av. Cel. Francisco Heráclito dos Santos, 210, Jardim das Américas, CEP 81531-990, Curitiba-PR, Brazil educividini@ufpr.br

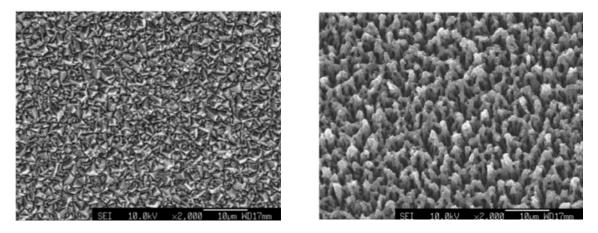
Graphene has exceptional properties such a high surface area, high light transmittance, high thermal stability, among others, which make it a potential candidate for nanocomposites synthesis. Nanoparticles of Ni(OH)<sub>2</sub> have received much interest due to their potential applications in several areas, such as sensors, magnetic devices, batteries, fuel cells, supercapacitors, etc. However, many studies show a low stability of this material during its application, leading to particle growth and/or changes in their crystalline structure. Thus, the synthesis of nanocomposites of Ni(OH)<sub>2</sub> nanoparticles supported on graphene offers many advantages as the maintaining of the morphology and crystalline structure of the nanoparticles and can give an improvement in other properties such as the conductivity of the material. Herein we report the synthesis and characterization of nanocomposites between reduced graphene oxide (rGO) and Ni(OH)<sub>2</sub> prepared by the polyol method. The synthesis of the nanocomposites was performed by heating a solution of graphene oxide (GO) and nickel acetate in ethylene glycol at 190 °C for 2 hours in a reflux system. Four different ratios of nickel salt and GO were used. After the reflux period, the material was filtered and washed. All nanocomposites and the materials obtained from synthesis made only with GO or Ni(OH)<sub>2</sub> were characterized by different techniques such as X-ray diffraction, Raman spectroscopy, UV-Vis spectroscopy, infrared spectroscopy (FT-IR), scanning electron microscopy, thermogravimetric analysis, X-ray spectroscopy (EDS) and cyclic voltammetry. The synthetic route used led to the reduction of GO to rGO and the defective α-Ni(OH)<sub>2</sub>, which is a very interesting structure for electrochemical applications. However, the variation of the GO: nickel salt ratio led to changes in the lamellar spacing of the Ni(OH)<sub>2</sub>, where smaller proportions of Ni<sup>+2</sup> led to a greater distance. The FT-IR and EDS spectra also indicated that ethylene glycol is acting as stabilizer of the Ni(OH)<sub>2</sub> nanoparticles. All the materials were used to prepare thin films by an interfacial system.<sup>[1]</sup> These thin films were electrochemical characterized in alkaline medium, where the number of cycling and the scan rate were evaluated. The change in the proportion of Ni(OH)<sub>2</sub> in nanocomposites also influence the electrochemical responses of such, where the nanocomposites with the 1:1 and 1:0.5 GO: nickel salt rates showed the higher responses.

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## High Surface Area Diamond Electrodes Templated by Vertically Aligned Carbon Nanotubes

Hudson Zanin, Paul W. May and <u>David J. Fermin</u> School of Chemistry, University of Bristol, Cantocks Close Bristol, BS8 1TS, UK david.fermin@bristol.ac.uk

Diamond based materials offer a high-performing dimensionally-stable platform for a large variety of applications in electrochemical sensing, energy conversion and water remediation [1]. Microwave plasma enhanced CVD diamond growth allows fine tuning crystal sizes from microcrystalline domains down to the so-called ultrananocrystalline films (grain sizes less than 10 nm). These methods generate surfaces with corrugations within the length scale of the mean grain size. More recent approaches have led to the fabrication of nanotube diamond structures with high aspect ratio via reactive ion etching of boron doped films.[2] This contribution will focus on an alternative approach employing vertically aligned carbon nanotubes (VACNT) as templates for the deposition of boron doped diamond (BDD) and diamond-like carbon (DLC) films. As illustrated in the figure, the VACNT template diamond films show a rich variety of microstructures [3,4]. Cyclic voltammetry and electrochemical impedance spectroscopy are used to investigate the activity of these films. It is shown that the electroactive area is over two orders of magnitude larger than conventional CVD grown diamond films. Interestingly, highly conducting DLC layers are obtained as-grown on the VACNT arrays in the absence heteroatoms acting as dopants [4].



Scanning Electron Micrographs of highly corrugated BDD films grown onto VACNT arrays [3].

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## Treatment and Electrochemical Performance of Recycled Graphite from Spent Li-Ion Batteries

Sergej Rothermel, Martin Grützke, Martin Winter, Sascha Nowak University of Muenster, MEET Battery Research Center, Institute of Physical Chemistry Corrensstraße 46, 48149 Muenster, Germany sergej.rothermel@uni-muenster.de

Over the last two decades the use of Li-ion batteries (LIBs) is constantly increasing. With regards to environmental and economical sustainability, the European Parliament and the Council established guidelines for the treatment and recycling of spent LIBs stated in the Battery Directive 2006/66/EC. Consequently, member states are obligated to set up collection and recycling systems. Also, battery manufacturers have to ensure a recycling efficiency of at least 50% referenced to the average weight of the battery components by the year 2016. In addition, the recovered materials have to be reprocessed in a production process for their original or other purposes.

Today the development of the recycling routes is primarily aimed at the recovering of the valuable components and materials such as Li, current collectors, transition metals from cathode materials and organic compounds from the electrolytes.[1] As a result of a high availability of graphite, the recycling of anodes is not in focus of interest so far. Taking into account that during the recycling process already solvent-free graphite is created as by-product and needs to be disposed, one has to consider whether the reprocessing of recycled graphite is more reasonable than its disposal effort.

In this work, commercial lithium-ion 18650 cells were dismantled after their cycling to 70% state of health (SOH). The electrolyte was extracted using an autoclave extraction technique with supercritical helium head pressure carbon dioxide (sc HHPCO<sub>2</sub>).[2] Furthermore, the electrochemical performance of extracted and heat treated graphite was investigated in a three-electrode setup with metallic lithium as counter and reference electrode using a carbonate based electrolyte. Also the influence of SOH on the discharge capacity and Coulombic efficiency of recycled graphite is examined. The morphology of extracted graphite was closely studied by SEM technique and the surface of graphite particles was characterized by BET measurements as well as XPS. In addition, different treatment methods are evaluated, in order to modify the surface of extracted graphite particles, to remove the binder, decomposition products of the electrolyte and the SEI.

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### Nanocarbons for optoelectronic applications

#### Dirk M. Guldi

Department of Chemistry and Pharmacy 7 Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universitaet Erlangen-Nuernberg, Egerlandstr. 3, 91058 Erlangen, Germany Email: dirk.guldi@fau.de

Carbon is the key to many technological applications that have become indispensable in our daily life. Altering the periodic binding motifs in networks of sp<sup>3</sup>-, sp<sup>2</sup>-, and sp-hybridized C-atoms is the conceptual starting point for a wide palette of carbon allotropes. To this end, the past two decades have served as a test-bed for measuring the physico-chemical properties of low-dimensional carbon with the advent of fullerenes (0D), followed in chronological order by carbon nanotubes (1D), carbon nanohorns, and, most recently, by graphene (2D). These species are now poised for use in wide-ranging applications.

Expanding global needs for energy have led to a significant effort to develop alternatives to fossil fuels. While alternative sources for energy are already in use, they comprise a small percentage of the energy demands needed to carry us through the 21st century. No single source will solve the global needs, but the development of photovoltaics has vast potential as a point-of-use power source. Recent work has shown that hybrid photoelectrochemical efforts with a percolation network of photon absorbers coupled to anelectron/hole transporter in combination with advanced photon management are the ideal design for realizing breakthroughs in high photon conversion efficiencies suitable for the catalysis of water.

I will report on our efforts regarding a unifying strategy to use the unprecedented charge transfer chemistry of OD fullerenes, the ballistic conductance of 1D carbon nanotubes, the semiconducting features of carbon nanohorns, and the high mobility of charge carriers in 2D graphene, together in a groundbreaking approach to solving a farreaching challenge, that is, the efficient use of the abundant light energy around us.

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## Superior Capacitance Behavior of Stacking Free Graphene Prepared by Glucose-assisted Freeze-drying Process

Bing-Joe Hwang<sup>a,b,\*</sup>, Ju-Hsiang Cheng<sup>a</sup>, Yi-Hsiu Chen<sup>a</sup>, Yun-Sheng Yeh<sup>a</sup>

<sup>a</sup>NanoElectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan. <sup>b</sup>National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan. 43 Keelung Road, Section 4, Taipei, Taiwan bjh@mail.ntust.edu.tw

The re-stacking of reduced graphene oxide (rGO) is the main reason to decrease its surface area and the capacitance. It was found that the re-stacking behavior highly correlates to the drying process and the glucose amount for the graphene oxide (GO) solution. The rGO/C composite is synthesized via heat-dry (HD) and freeze-drying (FD) processes separately and then a thermal reduction under 700 °C. The rGO/C composites are characterized by XRD, SEM, TEM and FTIR. The interspace of GO sheet increases as glucose amount increases for the freeze-drying process and the re-stacking could be reduced after thermal reduction. The capacitance is evaluated via cyclic voltammetry method which the rGO/C composite with freeze-drying and 1wt% glucose addition (FD-1%) could deliver highest capacitance 157.6 Fg<sup>-1</sup> at 5 mV/s scanning rate.

Keywords: Graphene, Glucose, Freeze-drying, Supercapacitor

## Electrochemical preparation of graphene-modified carbon felt electrodes for vanadium redox flow battery

P. Mazur<sup>1</sup>, J. Pocedic<sup>1</sup>, J. Vrana<sup>2</sup>, J. Dundalek<sup>2</sup>, J. Kosek<sup>2</sup>

 University of West Bohemia, Research Centre - New Technologies, Univerzitní 8, 306 14 Plzeň, Czech Republic mazurp@ntc.zcu.cz
 Institute of Chemical Technology Prague, Dept. of Chemical Engineering, Technická 5, 166 28 Praha 6, Czech Republic Juraj.Kosek@vscht.cz

The recent boom in the utilization of renewable energy sources with hardly predictable and controllable power production (e.g., wind turbines, photovoltaic cells) emphasizes the demand for efficient, cheap and reliable stationary energy storage technology. Among several possible candidates, vanadium redox flow battery (VRFB) exhibits several advantages such as: decoupled power and capacity, high efficiency of cycle, long durability and fast reaction time. The recent renaissance of the interest in the vanadium redox flow battery technology can be well illustrated by number of papers focused on the development of new membranes, electrodes, electrolyte additives, composite bipolar plates, stack designs and other particular solutions for the enhancement of the battery performance and decreased costs [1-3]. Despite the recent achievements, there is still a space for further optimization, especially with respect to the low intensity of the processes.

Our contribution aims to address the drawback of low process intensity by the development of enhanced carbon electrodes for the vanadium redox couples reactions. The specific surface area of the typically used carbon fiber felt was enlarged by its decoration by graphene-like structures. For that purpose we used the electrophoretic deposition coupled with subsequent electrochemical reduction of graphene oxide. Two methods of graphene oxide preparation were selected: i) chemical oxidation of graphite followed by ultrasonic exfoliation according to Hummers method [4] and ii) electrochemical preparation using surfactant assisted anodic oxidation of graphite [5]. On the prepared electrodes, the effect of surface functionalization on the reaction kinetics was studied by electrochemical oxidation in three-electrode arrangement. The structure and surface composition was characterized by SEM, XPS, *in-situ* Raman and  $\mu$ -X-ray tomography. The performance of the selected electrodes was tested in lab-scale VRFB single-cell.

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## Catalytic activity of MN4 catalysts adsorbed on carbon nanotubes towards O<sub>2</sub> reduction.

<u>F. Javier Recio</u>, Marco Viera, César Zúñiga, Ricardo Venegas, Cristian Gutiérrez, Federico Tasca, José H. Zagal

Facultad de Química y Biología, Departamento de Química de los Materiales, Departamento de Química de los Materiales. Chile

#### francisco.recio@usach.cl

In previous studies, we have established that the formal redox potential is a good reactivity index for the electrocatalytic activity of surface-confined metal phthalocyanines and metal porphyrins (MN4 complexes) toward the reduction of molecular oxygen [1]. Those experiments were performed with the MN4 adsorbed directly on edge plane graphite electrode. The results show a semi-volcano correlation that indicates that the catalytic activity of the complex increase when the potential of the redox couple associated to the catalytic process increase. According to those results the best strategy to increase the catalytic activity of the complexes is tuning their redox potential to more positive values by the chemical modification of the complex. A recent study performed with the same MN4 complex to the oxidation of cysteine have shown an increase of the catalytic activity and a change on the mechanism of cysteine oxidation when those these complex are preadsorbed on carbon nanotubes [2]. The present work studies the influence of the preadsorbed MN4 on carbon nanotubes towards the molecular oxygen reduction in basic media.

The experimental procedure are similar that to the previously described [2]. Multi-wall carbon nanotubes (MWCNTs) were dispersed in solutions of either phthalocyanines by sonication and were left to rest for 24 h at room temperature. After that, they were filtered and washed with DMF and ethanol to remove the excess of complexes that were not adsorbed on the surface of the nanotubes. The solid obtained was allowed to dry in an oven for 24 h. A new suspension was then obtained from the filtered MWCNTs+ MN4 (1 mg mL-1 in DMF) and used for the study. We have extended previous studies of those these correlations using several substituted phthalocyanines (MPcs) directly adsorbed on the edge plane of graphite and also preadsorbed on the MWCNTs.

The results show an increase of the activity towards the oxygen reduction reaction when MWCTs are employed, however, not significant change in the mechanism towards the oxygen reduction is observed. The results indicate that there are two ways to increase the catalytic activity: tuning the redox potential of MN4 to more anodic potentials and preadsorb the MN4 on carbon nanocomposites.

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## **Electrosorption on Carbon for Hybrid Aqueous Supercapacitors**

Krzysztof Fic, Mikolaj Meller, Elzbieta Frackowiak

Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry Berdychowo 4, 60965 Poznan, Poland krzysztof.fic@put.poznan.pl

Carbon occupies a prominent place in recent development of energy conversion and storage systems and there is no doubt that novel carbon materials as well as a good correlation between their microstructure, composition and physicochemical properties are crucial towards higher efficiency or cycle life of these devices.

Electrochemical capacitors are excellent devices for power demands but they suffer from low energy density. Specific energy of electrochemical capacitors might be improved by operational voltage increase and certainly carbon electrode has remarkable impact on it. Recent studies confirm that positive and negative electrode should reveal different textural properties, oxygen content and pore size distribution. Our investigations performed for negative electrode have demonstrated that the voltage range of this electrode might be shifted towards hydrogen evolution potential and even easily exceeding this value. It is noteworthy that the interactions between the electrode and electrosorbed hydrogen are the strongest in case of 6 mol/L KOH solution. Hydrogen stored in statu nascendi in the ultramicropores of the activated carbon keeps the potential of the electrode in deep cathodic region and allows to reach higher voltage of the total system. Additionally, faradaic type of electrochemical storage permits to benefit from additional capacitance of the electrode (ca. 30% prior to initial value). More detailed investigations were focused on the influence of carbon microstructure on self-discharge of the electrode (loss of electrosorbed hydrogen) - preliminary results confirmed that electrode should be polarized closely to the hydrogen evolution potential, and there is no direct influence of carbon porosity on the overpotential value. Probably in the cathodic reductive conditions, oxygen content in the electrode did not affect remarkably the electrode performance.

Typical oxidative working conditions of positive electrode resulted in a fast aggravation of the electrode material and significant capacitance fade in alkaline, neutral and acidic electrolyte, whatever type, especially for electrode with relatively high oxygen and micropore content. Briefly, the lowest overpotential of oxygen evolution (ca. 120 mV) was recorded in acidic electrolyte (1 mol/L  $H_2SO_4$ ) for carbon with major contribution of micropores, specific surface area of 2500 m<sup>2</sup>/g and ca. 4% of oxygen. In order to avoid electrolyte decomposition and to improve electrode potential window, several electrolytes with redox activity (e.g. based on iodides, vanadium or cerium) have been investigated. Results obtained suggest that redox activity of aforementioned species shifts the oxygen evolution potential towards higher value and prevents capacitance fade during cycling. The most recent studies suggest that electrolyte for positive electrode should retain the pH value during operation; in this case, the electrochemical response is sensitive for oxygen functionalities which might influence the pH value directly on the electrode/electrolyte interface.

Full physicochemical characterization of carbon materials, i.e., specific surface area and porosity measurements by nitrogen adsorption, type of functionalities by thermogravimetry coupled with mass spectrometry or by potentiometric titration with  $pK_a$  distribution as well as by Raman spectroscopy allowed to elucidate the electrochemical performance.

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## Development of a high energy AC/AC capacitor in aqueous electrolyte

François Béguin, Paula Ratajczak, Paulina Babuchowska, Qamar Abbas

Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry Berdychowo 4, 60-965 Poznan, Poland francois.beguin@put.poznan.pl

Most of the current research on supercapacitors is oriented to energy density enhancement, in order to broaden the spectrum of their applications. As given by formula  $E = {}^{1/2}CU^{2}$ , energy is highly depending on voltage U, the latter being controlled by the stability window of the electrolyte. Therefore, most of the commercially available systems use organic electrolyte, e.g., NEt<sub>4</sub>BF<sub>4</sub> in acetonitrile, allowing 2.7–2.8 V to be reached. Due to the relatively high cost of these devices and the environmental unfriendly character of organic electrolytes, alternative solutions such as use of protic electrolytes must be investigated.

Until recently,  $H_2SO_4$  and KOH were mainly considered as aqueous electrolytes for supercapacitors, giving voltages of 0.7–0.8 V. By the use of neutral alkali sulfate solutions, we have demonstrated voltages up to ca. 2 V for AC/AC capacitors<sup>1</sup>. Such high values are possible owing to the high overpotential for di-hydrogen evolution related to the pH increase in the porosity of the carbon negative electrode. This presentation will show the various steps in the development of a prototype, utilizing safe, cost effective and environmental friendly materials. For a system using an industrial activated carbon and stainless steel current collectors, a voltage of 1.6 V could be demonstrated in lithium sulfate electrolyte under long term floating<sup>3</sup>. Beside, in this presentation, we will show a strategy enhancing the capacitance through redox contributions at the carbon/electrolyte interface. Overall, the system reaches an energy density comparable to that of a capacitor operating with the same carbon in organic electrolyte.

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## New pre-lithiation strategies of the graphite anode in lithium-ion capacitors

<sup>1</sup>Pawel Jezowski, <sup>1</sup>Krzysztof Fic, <sup>2</sup>Olivier Crosnier, <sup>2</sup>Thierry Brousse and <sup>1</sup>François Béguin

<sup>1</sup>Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry Berdychowo 4, 60-965 Poznan, Poland <sup>2</sup>Institut des Matériaux Jean Rouxel - Université de Nantes Rue Christian Pauc - 44306 Nantes Cedex 3, France francois.beguin@put.poznan.pl

Recently, traditional electrical double-layer capacitors based on the use of an organic electrolyte and activated carbon electrodes seem to have almost reached their limits in terms of energy density. Therefore, for a number of applications, new systems being able to display much higher energy density, without sacrificing power must be explored. In this context, Lithium-ion capacitors (LIC) have been introduced few years ago; they implement activated carbon and intercalated graphite as positive and negative electrodes, respectively. The operation of LIC requires an initial step to pre-lithiate graphite, either from an auxiliary lithium source<sup>[1]</sup> or directly from the electrolyte<sup>[2,3]</sup>. Since both approaches are not completely satisfactory, research on alternative solutions is necessary. Another strategy consists in using sacrificial lithium oxide as lithium ions reservoir added to the positive electrode<sup>[4]</sup>.

In this presentation, we propose to use either non-stoichiometric lithium nickel oxide  $Li_{1-x}Ni_{1+x}O_2$  or an organic lithium derivative, which are no longer electrochemically active in the working voltage range from 2.0 to 4.3 V after the first lithium extraction. It will be shown that the composition of the composite positive electrode strongly influences graphite lithiation and further the cycle life and power density of the full cell.

Acknowledgements: The Foundation for Polish Science is acknowledged for supporting the ECOLCAP project realized within the WELCOME program, co-financed from European Union Regional Development Fund.

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### The Carbon/Iodide Interface in Protic Ionic Liquid for Capacitors

Elzbieta Frackowiak, Piotr Skowron, François Béguin

Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry Berdychowo 4, 60965 Poznan, Poland

elzbieta.frackowiak@put.poznan.pl

Among various energy storage systems, great interest is focused on electrochemical capacitors (ECs) because of their high power and long cycle life. The most typical devices operate through the charge/discharge of the electrical double-layer at the electrode/electrolyte interface in aqueous or organic medium as well as in ionic liquid. The capacitance can be significantly enhanced by quick redox reactions originating from the electrolyte species at the electrode/electrolyte interface, for example by using iodide salt aqueous solutions. However, in the latter case, the voltage of the system is limited to 1 V due do the low thermodynamic window of water. Therefore, we propose to investigate a possible extension of this window by using solutions of iodide salt (KI and in ionic liquids (ILs). Taking into account the size of ILs and iodide species, the porosity of activated carbon will play a crucial role.

The ILs selected were triethylammonium bis(tetrafluoromethylsulfonyl)imide [Et<sub>3</sub>NH]-[TFSI] and 1ethyl-3-methylimidazolium bis(fluorosulfonyl)imide [Emim]-[FSI]. Two iodides, triethylammonium iodide [Et<sub>3</sub>NH]-[I] or tetraethylammonium iodide [Et<sub>4</sub>N]-[I], were introduced in the ionic liquid at a concentration of 0.25 mol/L. Potassium iodide KI (0.2 mol/L) was also used for comparison. The electrochemical experiments as cyclic voltammetry, galvanostatic charge/discharge and impedance spectroscopy were conducted using a two-electrode cell construction. In some experiments, a silver wire was added as pseudo-reference to monitor the potential of individual electrodes. Activated carbon (AC) with high microporosity coated on aluminum foil from Batscap (France) was used as working and counter electrode. Glass microfiber paper (Whatman) was utilized as separator. Galvanostatic (0.2 A/g) cycling up to 1.8 V in two-electrode cell (Figure 1B) demonstrates a remarkable increase of capacitance when [Et<sub>3</sub>NH]-[I] is added to [Et<sub>3</sub>NH]-[TFSI], from 78 to 157 F/g. The voltammogram of figure 1A shows clearly that the increase of capacitance is caused by the positive electrode where faradaic processes occur.

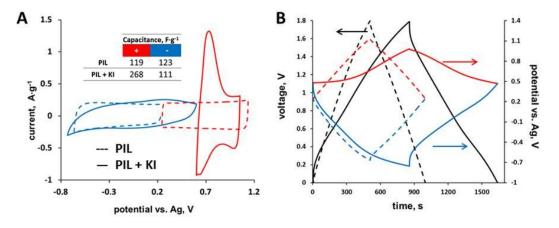


Fig. 1 Electrochemical properties in a symmetric AC/AC cell with Ag reference for the positive (red) and negative (blue line) electrodes recorded in  $[Et_3NH]$ -[TFSI] (dashed line) and 0.2 mol/L solution of KI in  $[Et_3NH]$ -[TFSI] (solid line): (A) cyclic voltammograms (2 mV/s); (B) galvanostatic (0.2 A/g) charge/discharge (the black lines are for the whole capacitor)

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### Oxygen plasma treated carbon electrodes for redox flow batteries

Ditty Dixon, Joachim Langer, Frieder Scheiba, Helmut Ehrenberg Research Scientist Karlsruhe Institute of Technology (KIT) Institute for applied materials- Energy storage systems (IAM-ESS) Hermann-von-Helmholtz-Platz 1 76344 Germany ditty.dixon@kit.edu

Redox flow batteries are gaining lot of attention these days as large scale electrical energy storage devices. Among them all vanadium redox flow batteries (VRB) are the most promising one as the cross contamination of the anolyte and catholyte spices are virtually solved by remixing of the electrolyte [1]. The capacity of the VRB depends mainly on the concentration and volume of the electrolyte or tank. However the practical capacity which can be delivered by the cell greatly depends on the activity of the electrodes. The activity of the electrodes in turns depends on the various functional groups such as –OH, - COOH present on the electrode surface. A balance between the amount of functional group and the extent of graphitization is extremely important as large amount of functional groups makes the electrode poor electrical conductor [2]. In this work commercially available graphite electrode felt are subjected to controlled oxygen plasma treatment. The plasma treated graphite shows excellent VRB performances in comparison with the conventionally heat treated electrode. When charged at constant voltage of 1.8 V, the electrolyte was charged much faster (or delivered high current) with plasma treated electrode when compared with conventional heat treated electrode. Moreover, the practical capacity of the cell was found to be highest for the plasma treated electrode when cycled galvanostatically at different current densities (fig 1).

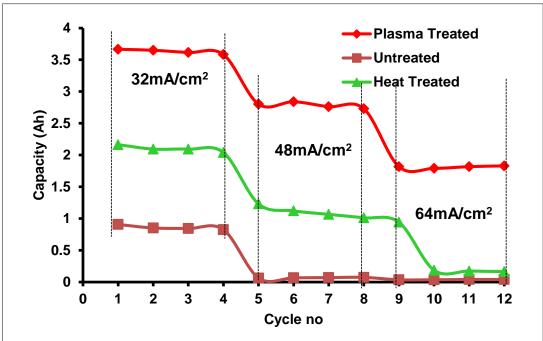


Figure 1. Garvanostatic cycling under different current densities

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## Tailoring the electronic conductivity in "brick and mortar" ordered mesoporous carbon – graphitic carbon nanostructures supercapacitor electrodes

Pasquale F. Fulvio, <sup>*a*, *b*</sup> Sheng Dai, <sup>*b*, *c*</sup> Xiqing Wang, <sup>*b*, *d*</sup> Richard T. Mayes, <sup>*b*</sup> Shannon M. Mahurin, <sup>*b*</sup> Bingkun Guo, <sup>*b*</sup> Xiao-Guang Sun, <sup>*b*</sup> Alex A. Puretzky, <sup>*e*</sup> Christopher M. Rouleau, <sup>*e*</sup> David B. Geohegan<sup>*e*</sup>

<sup>a</sup> Dept. Chemistry, University of Puerto Rico, Rio Piedras Campus, San Juan, Puerto Rico 00931. Fax: ++1-787-764-1588; Tel: ++1-787-764-0000 ext. 3505

<sup>b</sup> Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831.

<sup>c</sup> Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996. Fax: ++1-865-576-5235; Tel: ++1-865-576-7307

<sup>d</sup> Nanotek Instruments, Inc., Dayton, Ohio 45404.

<sup>e</sup> Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831.

pasquale.fulvio@upr.edu dais@ornl.gov

A general "brick and mortar" method for nanocomposites formed by ordered mesoporous carbon (OMC) "mortar" and various graphitic carbon "bricks" is reported. OMC composites were prepared using graphitic "bricks" such as graphene platelets (GnP), multi-walled carbon nanotubes (MWNT), single-walled carbon nanohorns (SWNH) and carbon black (CB). All materials have high specific surface areas raging from 350 to 700  $m^2/g$ , large uniform mesopores, and gravimetric capacitances exceeding 80 F/g in aqueous KOH. In this series, OMC-GnP materials display capacitance values comparable to OMC-MWNT composites in aqueous KOH, the lowest electrical series resistance (ESR) of ~0.17 Ohms and two distinct pore systems accessible for electrolyte diffusion. Despite the lowest ESR, the electrolyte diffusion was 5 times that of MWNT composites, but 6 times less than the reference OMC. A possible explanation is the large lateral grain size of graphene and of its composites, 25 µm, which may hinder diffusion. Hence, the "brick and mortar" method allows for the preparation of OMC composite supercapacitor electrode materials with tailored electronic conductivity and pore accessibility. These parameters are influenced by the graphitic "brick" nanostructure, size and final composite morphology.

## Reduced graphene oxide modified nanocomposites for solar water splitting

<u>Wei-Nien Su<sup>1</sup></u>, Andebet Gedamu Tamirat<sup>2</sup>, Abiye Kebede Agegnehu<sup>2</sup>, Amare Aregahegn Dubale<sup>2</sup>, Chun-Jern Pan<sup>2</sup>, Jyh-Fu Lee<sup>3</sup>, and Bing-Joe Hwang<sup>2,3</sup>

<sup>1</sup>NanoElectrochemistry Laboratory, Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan.

<sup>2</sup>NanoElectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan.

<sup>3</sup>National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.

43 Keelung Road, Section 4, Taipei, Taiwan

wsu@mail.ntust.edu.tw

Highly conductive reduced graphene oxide sheets are used to suppress the recombination of electron-hole for different transition oxide-based semiconductors in order to enhance the photocatalytic and photoelectrochemical performance under visible light. Porous vanadium-doped titanium oxide was prepared and hybridized with reduced graphene oxide sheets as nanocomposites. By comparing with nondoped and non-modified titanium oxides, it shows that the hydrogen evolution of the nanocomposite has been notably enhanced. Similarly, the photoelectrochemical activity of hematite is limited by poor charge-carrier separation efficiency due to fast electron-hole recombination. Here, reduced graphene oxide was also employed as an electron conducting scaffold into 3D urchin-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode for the photochemical water oxidation. The reduced graphene oxide modified  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructure was found to exhibit an enhanced photocurrent density (1.06 mA cm<sup>-2</sup> at 1.23 V vs. RHE), which is 1.47 times higher than that of pristine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. A two-fold enhancement in the photoconversion efficiency, resulting from the excellent electron gathering and transporting properties of reduced graphene oxide that efficiently lessens the recombination of charge carriers, was also noted. We have also found 16% enhancement in charge separation efficiency after Fe<sub>2</sub>O<sub>3</sub> photoanode was modified with reduced graphene oxide at 1.23 V versus RHE applied potential. Overall, these noble metal-free nanocomposite materials composed of highly conducting sheets loaded with stable, cheap and environmentally friendly transition metal oxide-based nanostructures offer a promising way of designing new photoelectodes with augmented performance.

## Glucose oxidizing anodes under physiological conditions: Using design of experiment to probe optimum combination of enzyme, mediator and support materials.

<u>Rakesh Kumar</u>, Isioma Osadebe, Peter Ó'Conghaile, Paul Kavanagh, Dónal Leech School of Chemistry & Ryan Institute, National University of Ireland, Galway, University Road, Galway, Ireland. r.kumar2@nuigalway.ie

The immobilisation of an enzyme and redox mediators on an electrode surface to provide an electrocatalytic biofilm is of critical importance for biosensor and biofuel cell development [1, 2]. Immobilisation can have a significant impact on the magnitude and stability of the electrochemical response [3]. The co-immobilisation of enzyme, multiwalled carbon nanotubes (MWCNTs), redox complexes and polymer support using a chemical crosslinker provides a 3-dimensional biofilm for electrocatalysis [1, 4]

Here, we report on enzyme electrodes composed of glucose oxidase enzyme, multiwalled carbon nanotubes and range of redox mediators and polymer support to improve the current density and stability of electrochemical cells. Enzyme electrodes are constructed using carbodiimide coupling of carboxymethyl dextran and acid treated multiwalled carbon nanotube to amine containing redox complexes and enzyme [5].

Further, we report on the optimization of electrochemical response of enzyme electrodes using a design of experiment approach, in seeking to further improve the current density under physiological conditions. The design of experiment model is validated and experimental results found to be largely consistent with the predicted values. Overall, a maximum current density of  $1.2 \pm 0.1$  mA cm<sup>-2</sup> or  $5.2 \pm 0.2$  mA cm<sup>-2</sup> at 0.2 V vs. Ag/AgCl, in pH 7.4 phosphate buffer at 37 °C containing 5 mM or 100 mM glucose, respectively, was achieved for oxidation of glucose using such biofilms incorporating MWCNTs, showing promise for application as an anode in a biofuel cell for electric power generation.

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# Electrochemical production of hydrogen peroxide: since the study of oxygen reaction reduction until H<sub>2</sub>O<sub>2</sub> generation in electrochemical flow reactor

Robson S. Rocha<sup>2</sup>, Ricardo B. Valim<sup>1</sup>, Jussara F. Carneiro<sup>1</sup>, Jonas B. Reis<sup>1</sup>, Leandro C. Trevelin<sup>1</sup>, Fernando L. Silva<sup>1</sup>, Willyam R. P. Barros<sup>1</sup>, Geiser G. Oliveira<sup>1</sup>, Rodnei Bertazzoli<sup>3</sup>, Mauro C. Santos<sup>4</sup>, Marcelo Zaiat<sup>2</sup>, Marcos R. V. Lanza<sup>1</sup>\*<sup>‡</sup>

1 - IQSC – Universidade de São Paulo (USP)<sup>‡</sup>
 2 - EESC – Universidade de São Paulo (USP)
 3 - FEM – Universidade Estadual de Campinas (Unicamp)
 4 - CCNH – Universidade Federal do ABC (UFABC)

<sup>‡</sup>Av. João Dagnone, 1100, CEP 13563-120, São Carlos, SP, Brazil / \*marcoslanza@iqsc.usp.br

#### Abstract

The electrosynthesis of hydrogen peroxide is an interesting technological process to produce one of the most versatile oxidizing substances, both for its industrial production as for its application in wastewater treatment processes. In this context, electrochemical technology offers an alternative for the  $H_2O_2$  generation at room temperature and low pressures without the use of catalysts in solution as commercial process and adds to these advantages the possibility to modify electrodic materials to achieve higher concentrations with lower energy consumption in aqueous media. The aim of this work has shown the evaluation results of carbon black activity, with and without modification by tertbutylanthraquinone (TBA) as carbon modifier, in sequential steps: (1) study of the oxygen reduction reaction by porous microlayer<sup>1</sup> method with rotating ring-disk electrode (RRDE) system and (2) the application of these results on the construction of Gas Diffusion Electrodes<sup>2</sup> (GDE) for generation of  $H_2O_2$  in electrochemical flow reactor.

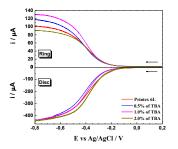


Figure 1: LSV of carbon black with and without 1% TBA. Potential range of +0.2 V to -0.8 V (vs. Ag/AgCl), 5 mV s<sup>-1</sup>. K<sub>2</sub>SO<sub>4</sub> 0.05 mol L<sup>-1</sup> (pH 2.0) solution.

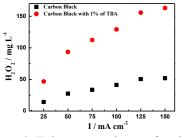


Figure 2:  $H_2O_2$  concentration as a function of applied current density at 1200 mL h<sup>-1</sup>.  $K_2SO_4$ 0.05 mol L<sup>-1</sup> (pH 2.0) solution.

Linear Sweep Voltammetry (LV) of the carbon black with and without modifier shown that the addition of 1% TBA increase the ring current of  $H_2O_2$  on the RRDE system, the behavior that may be associated with influence of the quinone group of the modifier, implying an electrochemical/chemical mechanism, where TBA is electrochemically reduced with sequential self-oxidation with chemically reduction of  $O_2$  (Figure 1). The results of  $H_2O_2$  generation in electrochemical flow reactor with GDE modified with 1% TBA (Figure 2) has shown that the modification of the GDE promoted an increase in the  $H_2O_2$  production reaching 160 mg L<sup>-1</sup> at 150 mA cm<sup>-2</sup>. These results prove the information of RRDE system, where the addition of TBA increases the generation of  $H_2O_2$ .

Acknowledgments: FAPESP, CNPq and CAPES for financial support. References: <sup>1</sup>Electrohim Acta 139 (2014) 1-6; <sup>2</sup>Ind. Eng. Chem. Res. 51 (2012) 649-654

## Functionalization of Macroscopic Carbon Materials Electrochemically Inducing Their Polyaromatic Reactivity

Viatcheslav Jouikov<sup>*a*</sup> and Jacques Simonet<sup>*b*</sup>

*a)* UMR 6226, CPM, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France b) Laboratoire MaSCE, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex,

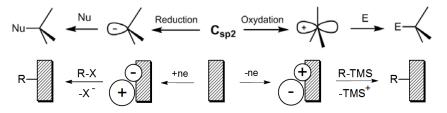
France.

e-mail: vjouikov@univ-rennes1.fr, jacques.simonet@univ-rennes1.fr

Technological carbons and carbon nano-forms (GC, HOPG, graphene, CNT) are often seen as materials almost devoid of own chemical reactivity. Their electrochemistry usually concerns reduction of remnant carboxy, carbonyl and epoxy groups [1] and a recent review stated that "graphite exhibits no inherent electrochemistry" [2]. Meanwhile, considering the  $C_{sp2}$  network of these materials it is surprising that while low-side aromatics are both reducible and oxidizable, these higher carbonaceous materials are not.

Considering this paradoxical situation, we recently demonstrated that cathodic charging of graphite, first reported in late 70's [3], is related to a massive electrochemical reduction of this material transforming it into a poly-nucleophilic reagent [4]. Since this process mostly affects the surface, such very reactive interfaces have been derivatized with a variety of electrophilic reagents (COOH, OOR, vinyl, ferrocenyl, trialkoxy silyl, silatranyl, 9,10-anthraquinonyl (AQ), 4-nitrobenzyl etc) practically filling the monolayer ( $\Gamma \approx 10^{-9}$  mol cm<sup>-2</sup>). Similar methodology was successfully applied for graphene modification, both as a standalone material [5] or deposited at a solid conductive support (GC, metals) [6,7]. In the last case, graphene can be *in situ* prepared and functionalized (e.g. with redox active markers such as ferrocene, anthraquinone, iodobenzene etc) in a one-step procedure. Dense carboxylation of graphene at a GC interface, via its cathodic charge in the presence of electrophilic CO<sub>2</sub> (grafting one COOH group per 35 phenyl units of graphene), enhances its hydrophilicity and permits further reactions with appropriate electrophiles [6] to give *p*-R-benzyl (R = NO<sub>2</sub>, I), AQ and H<sub>2</sub>N-AQ-modified graphene.

On the anodic side, the oxidation of graphite and GC at E = 1.5...2 V allows preparing polyelectrophilic highly reactive interfaces that can be functionalized using appropriate nucleophiles via an S<sub>E</sub>2-like process (e.g. Me<sub>3</sub>Si-substituted allyl and benzyl derivatives) providing a very high surface density of the grafted units, (7-9)×10<sup>-8</sup> mol cm<sup>-2</sup> [8].



Inherent unsaturation of carbon materials was further exploited with new methods of radical production in the vicinity of such interfaces. Thus, one-electron cleavage of C-I bonds (present as is or *in situ* formed by Br/I exchange [9]) was realized at carbon electrodes doped with sub-nanomolar amounts of transition metals (Pd, Pt, Au, Cu and Ni at  $\Gamma \approx 10^{-10...-9}$  mol cm<sup>-2</sup>) at -1.0 to -1.5 V vs. Ag/AgCl. Alkyl radicals thus produced permitted anchoring various functional groups (ferrocene, AQ, silatrane) to carbon interfaces with surface density of ca.  $5 \times 10^{-9}$  mol cm<sup>-2</sup> [9,10]. This methodology was successfully used for silvation (creating Si-C bonds) of carbon interfaces, one of less prone for silanization [11].

Preparation of these functionalized interfaces and examples of their use for catalysis, sensing and electrochemically addressed spin-writing will be presented.

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## Electrochemical Behaviour of Hybrid Devices Based on Alkaline Metal Salts in Neutral Aqueous and Non-Aqueous Electrolytes and Carbon Electrodes within Very Wide Cell Potential Region

Enn Lust, Alar Jänes, Jaanus Eskusson, Rait Kanarbik, Priit Möller, Ann Laheäär, Indrek Tallo, Heisi Kurig, Rasmus Palm, Ester Tee Institute of Chemistry, University of Tartu 14a Ravila Str., 50411 Tartu, Estonia Enn.Lust(@ut.ee

FIB-SEM, XPS, HRTEM, FIB-TOF-SIMS and Brunauer-Emmett-Teller gas adsorption methods have been used for the characterisation of physical properties of microporous carbide derived carbon electrodes, prepared from  $Mo_2C$  at 600, 800 and 1000 °C (noted as  $Mo_2C$ -CDC), before and after electrochemical tests conducted within very wide two electrode cell potential region. For more detailed analysis, the three-electrode cells have been completed and tested.

Cyclic voltammetry, constant current charge/discharge and impedance data have been analysed to establish the electrochemical characteristics of the hybrid devices consisting of the 1 M Na<sub>2</sub>SO<sub>4</sub> and 1 M Rb<sub>2</sub>SO<sub>4</sub> aqueous [1,2] and LiBF<sub>4</sub>, NaBF<sub>4</sub>, NaPF<sub>6</sub> and Cs-carborane non-aqueous [3-7] electrolytes and Mo<sub>2</sub>C-CDC electrodes within the very wide cell potential region ( $\Delta E \le 2.4$  V for H<sub>2</sub>O and  $\Delta E \le 4.5$  V for non-aqueous systems).

Influence of cation chemical composition and solvent properties (dielectrical constant, effective dipole moment and polarizability) on the electrochemical characteristics of supercapacitors/electrochemical hybrid devices has been established and analysed. Complex kinetic behaviour of completed devices (adsorption, blocking adsorption and intercalation of Li<sup>+</sup>, Na<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> ions, faradic charge transfer and mass transfer, gas adsorption, etc.) has been established at  $\Delta E \ge 1.5$  V for H<sub>2</sub>O and  $\Delta E \ge 3.6$  V for non-aqueous systems. At least three different characteristic time constants dependent on the electrolyte cation composition and cell potential applied have been established. Non-linear square root fitting analysis has been made and the results obtained have been discussed.

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## **Capacitive Charge Storage Behavior of Electrochemically Reduced Graphene Oxides Investigated By Fast Electrogravimetric Methods**

<u>Ozlem Sel</u><sup>1,2</sup>, Hubert Perrot<sup>1,2</sup>, Ivan T. Lucas<sup>1,2</sup>, Mohammed Lahcini<sup>3</sup>, Mustapha Raihane<sup>3</sup>, Abdelkrim El Kadib,<sup>4</sup> Hamza Goubaa<sup>1,2</sup>, Freddy Escobar<sup>1,2</sup>, Ibtissam Ressam<sup>1,2,3</sup>

<sup>1</sup>Sorbonne Universités UPMC Univ Paris 06, UMR 8235, LISE, F-75005, Paris, France <sup>2</sup>CNRS, UMR 8235, LISE, F-75005, Paris, France

<sup>3</sup>Laboratoire de Chimie Organométallique et Macromoléculaire Matériaux compostes, Faculté des Sciences

et Techniques, Université Cadi Ayyad, B.P 549 Marrakecch Morocco

<sup>4</sup>Euromed Research Institute, Engineering Division, Euro-Mediterranean University of Fes

(UEMF), Fès-Shore, Route de Sidi Hrazem, 30070 Fès, Morocco

E-mail: <u>ozlem.sel@upmc.fr</u>

Electric double-layer capacitors (DLCs), also called supercapacitors, store charges through reversible ion adsorption at electrolyte-electrode interfaces upon applying a voltage.<sup>1</sup> Carbon materials are known to be the most ideal as supercapacitor electrodes with their capacitance directly proportional to surface area and porosity. Among these carbons, graphene and graphene-like materials have shown great application potential. However, producing graphene with desirable properties is still a significant challenge. Synthesis route from graphene oxides (GO) is considered to be the most economical, but often includes hazardous chemicals. Therefore, electrochemical methods are often preferred as a green strategy for the reduction of graphene oxides to produce graphene-like materials.<sup>2</sup>

In this study, the capacitive charge storage behavior of electrochemically reduced graphene oxide (ERGO) was examined. GO films were elaborated on the gold electrode of a quartz resonator which was followed by a subsequent electrochemical reduction step. The reduced film was then characterized with structural characterization methods such as FEG-SEM, EDX, XRD, HR-TEM and in-situ Raman spectroscopy during electro-reduction of GO films. The supercapacitive charge storage was evaluated by classical electrochemical methods such as cyclic voltammetry in aqueous electrolytes. Since EDLCs store energy by accumulating positive or negative charges from electrolytes on the surface of the electrodes, the understanding of the dynamics of the ion transfer at the electrode/electrolyte interfaces is highly important to further improve the performance of these electrodes. Fast electrogravimetric methods, i.e. coupling fast quartz crystal microbalance (QCM) and electrochemical impedance spectroscopy (EIS) (acelectrogravimetry) have recently been employed for studying transfer and transport phenomena in materials for charge storage.<sup>3</sup> This coupled method, so called *ac*-electrogravimetry differs from classical EQCM and measures the usual electrochemical impedance,  $\Delta E/\Delta I$  ( $\omega$ ), and the mass variations of the film under a sinusoidal potential perturbation,  $\Delta m/\Delta E$  ( $\omega$ ), simultaneously.<sup>4</sup> This coupling has the ability to detect the contribution of the charged or uncharged species and to separate the anionic, cationic, and the free solvent contributions during the various (pseudo)capacitive processes. Under a potential perturbation, ERGO electrode mass varies due to the electroadsorption/desorption process at the electrolyte/film interface to ensure electroneutrality. This phenomenon was investigated with ac-electrogravimetry in various aqueous electrolytes (LiCl, NaCl and KCl, thus varying the cation size). Our findings indicate that there are two different charged species are transferred (solution cations and their hydrated counterparts) and free solvent molecules indirectly intervene in the charge compensation, suggesting a more complex charge storage behavior than envisaged. Our comparative study shows that the transfer of  $K^+$  cations is more rapid than that of Na<sup>+</sup>, and Li<sup>+</sup> ions are the slowest species transferred. This kinetic behavior can be attributed to the differences in the dehydration energies of the present cations. The transfer of  $K^+$  is faster, most likely due to its easier dehydration (easier removal of its hydration shell). In contrast,  $Li^+$  is strongly attached to its hydration shell, making its transfer slower. To the best of our knowledge, this study is the first experimental attempt to understand the ion transfer dynamics in ERGO by fast electrogravimetric methods, which might have significant implications on the supercapacitive charge storage mechanisms and to extract subtleties unreachable with classical tools.

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## Free-Standing Reduced Graphene Oxide Sheets Composites Supported onto 3D Matrix for different electrochemical applications

<u>Susana I. Córdoba de Torresi</u><sup>a</sup>, Vinicius R. Gonçales<sup>b</sup>, Jadielson L. Antonio<sup>a</sup>, Rafael N. P. Colombo<sup>a</sup>, Marco A. de O. Minadeo<sup>a</sup>, Elaine Y. Matsubara<sup>c</sup>, José M. Rosolén<sup>c</sup>

<sup>a</sup>Instituto de Química, Universidade de São Paulo, POBox:26077 – Cidade Universitária, São Paulo – SP – Brazil.

<sup>b</sup>School of Chemistry, University of New South Wales, Room 126 Dalton Building, F12 – Kensington, Sydney, NSW – Australia

<sup>c</sup>Departamento de Química-FFCLRP, Universidade de São Paulo, 14040-901, Ribeirão Preto-SP- Brazil

This work presents two novel 3D carbon composite electrodes containing free standing reduced grapheme oxide. The first one consists of reduced graphene oxide (RGO), carbon nanotubes, and carbon fiber felt. In this matrix, the basal planes of the micrometer scale RGO sheets are not in contact with the felt. The edges of these electron transparent RGO sheets are, in fact, bound to cup-stacked carbon nanotubes (CSCNTs) deposited on the carbon microfibers of the carbon felt, as depicted in Figure 1.

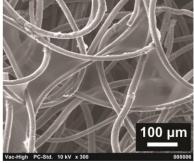




Figure 1 – FESEM image of 3D composite carbon felt with free-standing RGO basal planes(left) and Ppy-HS/GO (right).

The available surface area and the presence of free-sating RGO sheets in which  $\pi$  orbitals of the basal planes do not interact with the electrode offers a huge advantage to the study of demanding bioelectrochemical reactions, such as the FADH<sub>2</sub>/FAD redox transition often claimed in literature as originated from a direct electron communication between micro/nano carbon based electrodes and glucose oxidase (GOx). In order to discuss the possibility of a direct electron transfer with GOx, results were confronted with the achieved by immobilizing free FAD residues on the same 3D composite matrices. This comparison is a relevant and still open issue that suffers lack of investigation in the literature.

Figure 1 also shows the second matrix Ppy-HS/GO composite, with 3D open structure where the GO sheets are found scattered between the Ppy microfibers. The synthesis of this material consists in the polymerization of the pyrrole (Py) monomer in 5 mM methyl orange (MO) aqueous solution at pH 2. In this solution, the GO is dispersed under ultrasonic stirring during 2 hours. Then, the polymerization could be performed chemically or electrochemically by oxidation of the Py monomer. The methyl orange plys the role of a template system to get Ppy at microfibrillar shape, which is fundamental to form the hydrosponge structure. The Ppy-HS/GO material can be potentially applied as a supercapacitor. Its large superficial area provides a synergism t between the high capacitance of Ppy and high cycling stability of GO. The conducting properties of the Ppy-HS/GO could be improved by reduction process of GO and changing the Ppy/GO ratio.

#### Diamond anodes for electrolysis of wastewater: key material or fake?

J.F. Pérez-Serrano, M.J. Martín de Vidales, S. Cotillas, J. Llanos, C. Sáez, <u>M.A. Rodrigo</u>, P. Cañizares Department of Chemical Engineering. Faculty of Chemical Sciences and Technologies. University of Castilla La Mancha. Campus Universitario s/n 13071 Ciudad Real. SPAIN Manuel.Rodrigo@uclm.es

During the recent years, many studies have been carried out on the treatability of wastewater using diamond electrodes. Both, synthetic and actual wastewater, have been used and it has been demonstrated the efficiency of the process in terms of energy consumption and the robustness of the technology in terms of the wide variety of sources studied with excellent treatment outcomes.

This lecture aims to summarize the state of the art of the technology based on the experience of the authors with this advanced carbon material. To do this, results obtained in our lab on the treatment of different types of actual wastewater coming from different sources (fine chemicals, food processing, metalworking, pesticides ...) are analyzed, pointing out the advantages and drawbacks of the technology by comparing results obtained by the electrolytic technology with those obtained using other advanced oxidation processes, widely applied in the industry nowadays. Special attention is paid to production of intermediates, maximum mineralization that can be attained, improvement in biodegradability and economy. It is also discussed the causes which explain why, after two decades of exhaustive research and development, this technology is not widely applied at the industrial scale nowadays (prize of diamond, lack of suppliers, uncertainly about performance within industrial environment, lack of life-test, improper applications, etc.). The lecture also faces the challenges of the technology for the near future (electrode manufacturing, reactor engineering, coupling with irradiation technologies, scale-up, cost optimization...) pointing out the direction in which research and engineering studies have to be carried out in order to attain attractive processes which could be implemented at the industrial scale.

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## Multiscale modeling of lithium sulfur battery involving cathode carbon microstructure

Kan-Hao Xue,\* Mathieu Morcrette, Claude Guéry and Alejandro A. Franco\*\*

<sup>1</sup>Laboratoire de Réactivité et Chimie des Solides, UMR CNRS 7314, Université de Picardie Jules Verne 33 rue Saint Leu, 80039 Amiens Cedex, France <sup>2</sup>Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France

Siberage Lieen benimique de l'Energie (RS2E), I'R CIARS 5459, I'rance

\* <u>kanhao.xue@u-picardie.fr</u> \*\* <u>alejandro.franco@u-picardie.fr</u>

Lithium sulfur (Li/S) battery is a strong candidate for high density energy storage due to its 1675 mAh/g (in sulfur mass) theoretical capacity and reported 1320 mAh/g experimental capacity,<sup>[1]</sup> as well as its low material cost. Capacity degradation and polysulfide shuttle induced self-discharge are the two main hindrances to its commercialization. Multiscale computational models may provide helpful insights into the battery operation principles and degradation mechanisms.<sup>[2]</sup> However, only very few models have been reported so far for Li/S battery and none of them considers the influence of the cathode microstructure.<sup>[3,4]</sup> Actually, it has been demonstrated that the utilization of highly ordered nanostructured carbon as the cathode platform may lead to a significant enhancement of the discharge capacity of Li/S battery models, which could provide useful feedbacks into the cathode optimization.

Here we propose a multiscale discharge model for Li/S batteries with particular focus on the role of the carbon microstructure in the overall cell response. We extend here the model previously proposed by Kumaresan *et al.*<sup>[3]</sup> by explicitly accounting for the ways that Li<sub>2</sub>S can precipitate into the cathode pores, and electronic tunneling effects. We provide a framework which allows for investigating the effect of different carbon pore size distributions and Li<sub>2</sub>S growth mechanisms.

Simulation reveals that solid sulfur was fully dissolved before the massive precipitation of  $Li_2S$ , therefore the critical microstructure influencing  $Li_2S$  precipitation is that of carbon, rather than sulfur. This is consistent with the fact that different carbon materials could lead to quite diverse discharge capacities. The treatment of  $Li_2S$  morphology in generally allows for thin film formation onto the carbon surface, or bulk/nanosized  $Li_2S$  particles through solution phase nucleation, similar to our previous modeling work on lithium air batteries.<sup>[5,6]</sup> A typical discharge curve by assuming fully thin film precipitation is shown in Fig. 1, where the maximum  $Li_2S$  thin film thickness is assumed to be 5 nm because of electron tunneling distance limitations. A compromise is seen for the choice of carbon pore size: too large pores are less in surface area, therefore leads to fast thin film growth, causing severe electron transport limitations; too small pores suffer from choking, while still being far from the electron transport limitations. This shows that an optimized carbon structure is crucial to the discharge performance of Li/S batteries.

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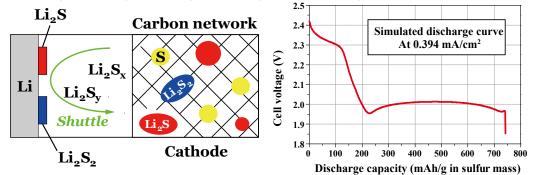


Figure 1. Schematic illustration of a Li/S battery and the corresponding discharge curve by mathematical simulation.

## Production of Porous carbons based on graphene foam-PVA/phenolformaldehyde composite as electrode material for supercapacitors

<u>Bello Abdulhakeem</u>, Barzegar Farshad, Momodu Damilola, Taghizadeh Fatemeh, Dangbegnon Julien, Manyala Ncholu

Department of Physics, Institute of Applied Materials, SARChI Chair in Carbon Technology and Materials, University of Pretoria, Pretoria 0028, South Africa. Corresponding author. E-mail address: bellohakeem@gmail.com

#### ABSTRACT

In the emerging field of energy storage technology and efficient economy depends on the ability to develop novel smart materials with excellent characteristics for electrical energy storage and delivery. The design and development of porous carbon electrode materials with suitable distribution of micro, meso and macro for electrical double layer capacitors (EDLC) to improve its energy storage efficiency to meet the increasing demand for renewable and sustainable energy resources is highly desirable due to the fact that the performance of these devices is closely related to material properties used for the fabrication of the device [1-4]. In this work we report on a two-step green chemistry synthesis of highly porous carbon structures, using a microwave irradiation process to produce a hydrogel based on graphene foam by the addition of polyvinyl alcohol (PVA), polypyrrole (PPY), phenol and formaldehyde. This was followed by activation with KOH and carbonisation of the hydrogel in the in the presence of argon gas at 800 °C for 60 minutes to produce the porous carbons. Morphological characterization reveals that the produced sample consists of highly dense packed cavities. The physicochemical properties of the electrolyte ion (diffusion) and it's influence on the capacitive behavior of the porous materials were elucidated. The electrochemical characterizations including cyclic voltammetry (CV), constant current experiment (charge-discharge) and long term cycling (stability) using a 6 M KOH aqueous electrolyte show that symmetric electrochemical double layer capacitor of these materials demonstrated a good capacitive performance exhibited a specific capacitance in the range of 150-170 F g<sup>-1</sup>, phase angles of 81° and 84° respectively with 98% retention of initial capacitance after 5000 cycles.

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## Electrocatalytic oxidation of methanol at PtRu nanoparticles supported on nitrogen doped carbon nanotubes

Tharamani Chikka Nagaiah<sup>a,\*</sup>, Wolfgang Schuhmann<sup>b</sup>, Chen Jin<sup>c</sup>, Martin Muhler<sup>c</sup>,

<sup>a</sup> Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar-140001, Punjab, India

<sup>b</sup>Elektroanalytik & Sensorik, <sup>b</sup> Laboratory of Industrial Chemistry, Ruhr-University Bochum, D-44780 Bochum, Germany

\*Corresponding author email address: <u>tharmani@iitrpr.ac.in</u>

Direct methanol fuel cells (DMFCs) are considered to be one of the most promising lowtemperature green power sources for automobiles and portable electronic devices due to their high energy density, low operating temperature and ease of handling of the liquid fuel. The basic principle employed in DMFCs involves oxidation of methanol at the anode and oxygen reduction at the cathode at precious metal catalyst such as platinum and platinum-ruthenium catalyst dispersed at a carbon support. Among many practical obstacles to commercial applications of these DMFCs, the insufficient catalytic activity and durability of the used electrocatalysts, of the carbon support and the dispersion of the catalyst particles at the supporting material are the main concerns to enhance the catalytic activity. Recently carbon nanotubes (CNTs) were identified as potential supporting material due to their good electron conductivity, high external surface area and stability. However, CNTs needs suitable chemical modifications to achieve good interaction with the catalytically active deposited metal particles.

In this respect, we are modifying the CNTs by introducing different nitrogen functional groups. In our studies, we have synthesized nitrogen-doped CNTs (NCNTs) by treating HNO<sub>3</sub>-oxidized CNTs (OCNTs) in an NH<sub>3</sub> flow at different temperatures. These NCNTs were used as a support for PtRu particles. The PtRu catalysts were prepared by an impregnation-reduction method from chloride precurors with a total metal loading of 10 wt%. The electrocatalytic activity with respect to methanol oxidation was studied using cyclovoltammetry (CV) and chronoamperometry and CO stripping measurements. The obtained catalysts materials show better activity and stability compare to PtRu/OCNT (Fig. 1). The TEM, XRD and XPS were employed to evaluate the morphology, microstructure and quantitatively identify different nitrogen functional groups and to evaluate their role for the observed enhanced catalytic activity. The local catalytic activity of methanol oxidation was visualized using scanning electrochemical microscopy as shown in Figure 2.

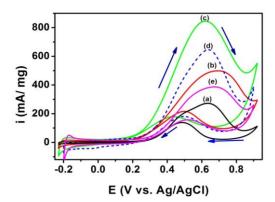


Figure 1. Cyclic voltammogram for methanol oxidation over PtRu supported on (a) OCNT, (b) NCNT-200 (c) NCNT-400 (d) NCNT-600 and (e) NCNT-800 in 1M CH<sub>3</sub>OH+0.5 M  $H_2SO_4$  at a scan rate of 5 mV/Sec

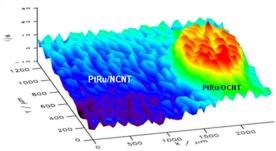


Figure 2. (A) RC-SECM 3D-images of PtRu/OCNT and PtRu-NCNT-400 catalyst spots in 1 M CH<sub>3</sub>OH+0.5 M H<sub>2</sub>SO<sub>4</sub> at a applied substrate potentials of 0.3 V. The tip (Pt-microelectrode, 25  $\mu$ m) was polarized at + 50 mV during P1 and at 400 mV during P2. Images taken after 288 ms of the detection pulse.

## Specific Electrolyte Additives for Non-Aqueous Carbon Based Supercapacitors

<u>Alar Jänes</u>, Jaanus Eskusson, Thomas Thomberg, Enn Lust Institute of Chemistry, University of Tartu 14a Ravila Str., 50411 Tartu, Estonia alar.janes@ut.ee

Microporous carbon electrodes based supercapacitors (SCs) with better performance and long-lasting cyclability are big interest for electric vehicle producers. However, very important problem is associated with the development of non-aqueous electrolytes with designed properties obtaining the characteristic relaxation frequencies, energy and power densities and other characteristics of SCs. The energy and power densities and other characteristics of SCs. The energy and power density and coulombic efficiency depend crucially on the region of ideal polarizability of the interface between the microporous carbon electrode and non-aqueous electrolyte solution. The replacement of acetonitrile (AN) with less harmful and less flammable solvent or mixtures of non-aqueous solvents is a very important step for the wide commercialization of SCs, because the AN is a toxic solvent and cannot widely used for the production of SCs for the consumer goods and computer back-up systems, as well as for other various peak power generation systems.

One possibility to increase the conductivity and decrease the viscosity of electrolyte is to use some specific electrolyte additives or so-called co-solvents [1, 2]. Many studies were performed on the optimization of the lithium-ion battery electrolytes using solvent mixtures. Cyclic propylene carbonate (PC) and ethylene carbonate (EC) have a high dielectric constant, good compatibility with carbon electrodes and it enables the dissolution of salts up to sufficient concentrations. However, these electrolytes are highly viscous and give poor conductivity even at ambient temperatures. When PC or EC is mixed with linear alkyl carbonates, more rapid ion transport is achieved as a result a lower viscosity and subsequently the higher ionic conductivity is achieved [1-3]. The resulting binary or ternary mixed solutions are widely used in commercially available lithium ion batteries. It was demonstrated that the choice of co-solvent is a critical issue that significantly effects not only the conductivity, but also the electrochemical performance, including the physicochemical properties of solid electrolyte interface formation. In recent years, fluoroethylene carbonate (FEC), diethyl sulfite (DES) and 1,3-propylene sulfite (PS) have been studied as a film forming additives for electrolytes in lithium ion batteries [4].

In this work the electrochemical characteristics of SCs consisting of the mainly microporous titanium carbide derived carbon (TiC-CDC) electrodes in 1 M ( $C_2H_5$ )<sub>3</sub>CH<sub>3</sub>NBF<sub>4</sub> solutions in propylene carbonate (PC), and mixtures of PC with FEC, DES and PS at different volume ratios have been studied using cyclic voltammetry, electrochemical impedance spectroscopy, constant current charge/discharge and constant power methods. The specific capacitance, phase angle, characteristic relaxation time constants and other values, dependent on the solvent system used and temperature applied, have been established. The region of ideal polarizability up to  $\Delta E \ge 3.2$  V has been demonstrated for TiC-CDC electrodes in all mixed non-aqueous electrolytes within the wide temperature region investigated. Specific conductivity values have been obtained and correlated with the electrochemistry including energy and power density data. It was concluded that the limiting capacitance, the characteristic time constant and complex power and energy values calculated depend noticeably on the solvent mixture used, i.e. on the specific conductivity of electrolyte solution [5, 6].

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## Boron Doped Diamond Electrode: Spectro/Photo/Electrochemistry and Prospective Application in Dye-Sensitized Solar Cell

L. Kavan<sup>1</sup>; Z. Vlckova-Zivcova<sup>1</sup>; H. Krysova<sup>1</sup>; V. Petrak<sup>2</sup>; J. Barton<sup>3</sup>; P. Cigler<sup>3</sup>; M. Nesladek<sup>4</sup>

<sup>1</sup>J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague 8, Czech Republic.

<sup>2</sup> Institute of Physics, v.v.i., Academy of Sciences of the Czech Republic Na Slovance 2, 182 21, Prague 8, Czech Republic

<sup>3</sup> Institute of Organic Chemistry and Biochemistry, v.v.i. Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 166 10 Prague 6, Czech Republic.

<sup>4</sup> IMEC, IMOMEC Division, University Campus Hasselt, Wetenschapspark 1, B-3590 Diepenbeek,

Belgium

Ladislav.Kavan@jh-inst.cas.cz

Spectral sensitization of wide band-gap semiconductors to visible light is intensively studied in the area of n-doped electrode materials, such as  $TiO_2$ . Attempts to sensitize p-type semiconductors (like NiO) are less frequently encountered in the literature, and the reported efficiencies are still low, compared to those of the n-type semiconductors used in dye-sensitized solar cells (DSCs). The final goal is obviously a tandem device (p,n-DSC) in which both electrodes are photoactive semiconductors. The B-doped nanocrystalline diamond (BDD) can be considered a promising alternative of p-NiO. Diamond films are attractive by their excellent chemical and electrochemically stability, optical transparency and favorable electrical properties. The electrochemical inertness of BDD is beneficial in view of the corrosive nature of certain electrolyte solutions used in DSCs. Nanocrystalline boron doped diamond films were grown by a microwave plasma enhanced chemical vapor deposition.[1,2] Electrochemical impedance spectroscopy provided the flatband potentials and concentrations of acceptors, which relate to the B-concentrations from the neutron depth profiling and from Raman spectroscopy (frequency of the 500 cm<sup>-1</sup> mode). Electrochemical cleaning of the surface from sp<sup>2</sup> carbon impurities was demonstrated by Raman spectroscopy.[1] The in-situ Raman spectroelectrochemistry in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> allows selective addressing of the modes of sp<sup>2</sup> impurities in the region of 1430–1610 cm<sup>-1</sup>. While the Raman response of sp<sup>3</sup> carbon is intact to electrochemical charging, the D, G and D' Raman modes of sp<sup>2</sup> carbon are not. The quality of nanocrystalline diamond electrodes can be thus analyzed in detail. Spectral sensitization of the nanodiamond surface was carried out by anchoring of dyes like 4-(bis-{4-[5-(2,2-dicyano-vinyl)thiophene-2-yl]-phenyl}-amino)-benzoic acid (P1 from Dyenamo AB). In a two-step procedure, polyethyleneimine is adsorbed on hydrogenated diamond surface and subsequently modified with P1. The sensitized diamond exhibits stable cathodic photocurrents under visible light illumination in aqueous electrolyte solution with dimethylviologen serving as electron mediator.[3] In spite of the simplicity of the surface sensitization protocol, the photoelectrochemical performance is similar or better compared to that of other sensitized diamond electrodes which were reported in previous studies (2008-14).[4]

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## Optimization of the binder concentration in the hierarchically microporous – mesoporous carbon catalyst layer

Eneli Härk<sup>1,2</sup>, Rutha Jäger<sup>2</sup>, Enn Lust<sup>2</sup>

<sup>1</sup>Soft Matter and Functional Materials, Helmholtz Zentrum Berlin, Hahn-Meitner-Platz 1, 14109, Berlin,

Germany

<sup>2</sup>Institute of Chemistry, University of Tartu, 14a Ravila Str. 50411, Tartu, Estonia

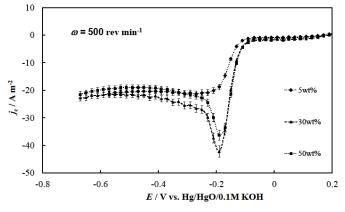
eneli.haerk@helmholtz-berlin.de

An intensive research has focused on the development of electrocatalyst for the oxygen electroreduction reaction (ORR) because in a polymer electrolyte fuel cell the major limit on performance is the slow oxygen electroreduction process. The oxygen diffusion within the catalyst layer is one of the key parameters and the Nafion® content probably determines the mass transfer rate in the catalyst layer. Preliminary results have been shown that due to the differences in the properties of the carbon support for catalysts, such as specific surface area, porosity, electrical conductivity, the oxygen electroreduction activity could be also influenced by the loading of the additive, commonly Nafion® binder. Therefore, the influence of Nafion® loading into the hierarchically microporous-mesoporous carbon catalyst layer of cathodes has been investigated (**Table**). The electrocatalysts with various Nafion® loadings (from 5 to 50 wt%) were studied applying the rotation disc electrode and cyclic voltammetry methods in 0.1 M KOH solution (**Figure**). It has been recognized that, the optimum Nafion® loading depends on the platinum content in the catalyst material, varying from 30 to 36 wt%.

Raman spectroscopy, XRD, SEM-EDX, HRTEM methods were applied for the structural and electronic characterization of materials. Gas adsorption at liquid nitrogen temperature was used for the porosity analysis of materials under discussion given in **Table**.

**Table**. Results of sorption measurements.  $S_{\text{BET}}$  – BET surface area,  $S_{\text{micro}}$  – micropore area, calculated using t-plot method,  $V_{\text{micro}}$  – micropore volume,  $V_{\text{tot}}$  – total pore volume.

Sample	$S_{\rm BET}$ / m <sup>2</sup> ·g <sup>-1</sup>	$S_{\rm micro}$ / m <sup>2</sup> ·g <sup>-1</sup>	$V_{\rm micro}$ / cm <sup>3</sup> ·g <sup>-1</sup>	$V_{\rm tot}$ / cm <sup>3</sup> ·g <sup>-1</sup>
C(Mo <sub>2</sub> C)	2057	1420	1.03	2.44
C(Mo <sub>2</sub> C) with 5 wt% Nafion®	1353	945	0.73	1.68



For microporous – mesoporous amorphous carbon material  $C(Mo_2C)$  impregnated with 30wt% Nafion® in catalyst layer showed higher activity toward ORR compared to the catalyst with 5 wt% Nafion®. Somewhat more positive half-wave potential value for 30 wt% compared with 50 wt% Nafion® binder has been established.

**Figure.** Rotating disk electrode data for ORR (corrected for current densities in 0.1 M KOH solution

saturated with Ar) for C(Mo<sub>2</sub>C) electrodes with various Nafion® loadings (noted in figure) in 0.1 M KOH solution saturated with O<sub>2</sub> (electrode potential scan rate  $v = 10 \text{ mV} \cdot \text{sec}^{-1}$ ; rotation speed 500 rev min<sup>-1</sup>). Acknowledgements

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## Kinetics of the Oxygen Electroreduction at Carbon Supported Noble and Non-noble Metal Nanoparticles Activated Electrodes

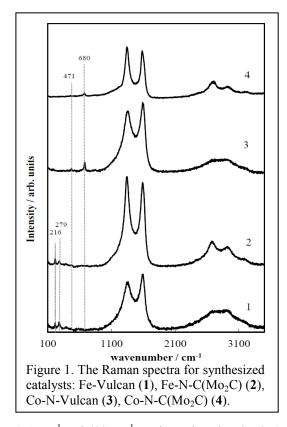
Rutha Jäger<sup>1</sup>, Eneli Härk<sup>1,2</sup>, Tavo Romann<sup>1</sup>, Enn Lust<sup>1</sup>

<sup>1</sup>Institute of Chemistry, University of Tartu, 14a Ravila Str. 50411, Tartu, Estonia

<sup>2</sup>Soft Matter and Functional Materials, Helmholtz Zentrum Berlin, Hahn-Meitner-Platz 1, 14109, Berlin,

Germany

rutha.jager@ut.ee



471 cm<sup>-1</sup> and 680 cm<sup>-1</sup> can be assigned to  $Co_3O_4$  (Figure 1, line 3 and 4).

The half-wave potential,  $E_{1/2}$ , i.e., catalytic activity of the composite catalyst is shifted toward more positive potentials in the following order: Fe-Vulcan < Co-N-Vulcan < Co-N-C(Mo<sub>2</sub>C) < Fe-N-C(Mo<sub>2</sub>C) < Fe-N-C(Mo<sub>2</sub>C) (Figure 2).

#### Acknowledgements

This work was supported by the Estonian target research: IUT20-13; the Estonian Centre of Excellence in Science Project: TK117T; the Estonian Energy Technology Program: SLOKT10209T; the Materials Technology: SLOKT12180T and by the European Spallation Source Project: Estonian Partition in ESS Instrument design, development and building and application for scientific research: SLOKT12026T. **References** 

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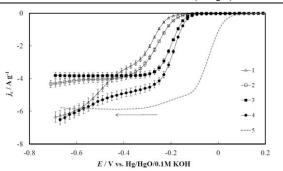


Figure 2. RDE data for electrocatalysts Fe-Vulcan (1), Co-N-Vulcan (2), Co-N-C(Mo<sub>2</sub>C) (3), Fe-N-C(Mo<sub>2</sub>C) (4) and Pt-C(Mo<sub>2</sub>C) (5) in 0.1 M KOH solutions saturated with O<sub>2</sub> (at electrode potential scan rate  $v = 10 \text{ mV} \cdot \text{sec}^{-1}$  and at rotation speed 3000 rev min<sup>-1</sup>).

The replacement of platinum or platinum group metals by low cost d-metal catalysts reduces overall cost of the polymer electrolyte fuel cell. Novel electrochemically active and inexpensive cathode materials basically consist of transition metal, nitrogen and carbon. The electrocatalysts derived from pyrolysis of iron or cobalt porphyrines or/and phtalocyanines have been investigated by the several researcher groups.

The series Fe-N or Co-N nanoparticles modified catalysts were synthesized by sodium borohydride reduction method, using respective inorganic nitrogen containing precursor salts. The effect of Fe-N or Co-N catalytic activity on the oxygen reduction reaction kinetics was studied in 0.1 M KOH aqueous solutions.

Electrochemical characteristics for nanoparticles activated carbons (Vulcan, C(Mo<sub>2</sub>C)) have been established by cyclic voltammetry and rotating disc electrode methods. For structural characterization of the materials XRD, Raman Spectroscopy, TOF-SIMS and SEM methods have been applied.

The Raman spectra of the iron nanoclusters deposited onto carbon support (Figure 1, line 1 and 2) have sharp bands at 216 and 279 cm<sup>-1</sup> corresponding to the alpha-Fe<sub>2</sub>O<sub>3</sub>. The bands with low intensities at gure 1, line 3 and 4).

## Modification of Edge and Basal Plane Graphitic Carbon using Aryldiazonium Salts: Chemisorption vs Physisorption

<u>Alison J. Downard</u>,<sup>1,2</sup> Lita Lee,<sup>1,2</sup> Paula A. Brooksby,<sup>1,2</sup> Anna Farquhar,<sup>1,2</sup> Haifeng Ma,<sup>1,3</sup> Simon A. Brown,<sup>1,3</sup> Yann Leroux,<sup>4</sup> Philippe Hapiot<sup>4</sup>

<sup>1</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand; <sup>2</sup>Department of Chemistry, <sup>3</sup>Department of Physics and Astronomy.

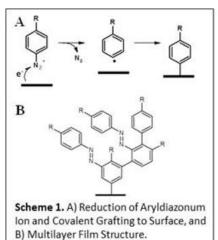
<sup>4</sup>Université de Rennes 1, Institut des Sciences Chimiques de Rennes (Equipe MaCSE), CNRS, UMR 6226, Campus de Beaulieu, Bat 10C, 35042 Rennes Cedex, France

Corresponding author: Email <u>alison.downard@canterbury.ac.nz</u>

Aryl radicals, generated by reduction of aryldiazonium salts, have become a popular reagent for modifying a wide range of conducting, semiconducting and insulating materials with nanoscale organic films (Scheme 1A). The interest in this approach mainly comes from the possibility of formation of a stable covalent bond between the modifier and the substrate, the wide substrate applicability and the ease of introducing different R groups to a surface.[1]

Much work has focused on modification of  $sp^2$  carbon materials by reduction of aryldiazonium salts. At glassy carbon, an essentially 100 % edge plane material, the formation of covalent bonds to the surface is well-established. However at basal plane materials such as highly ordered pyrolytic graphite (HOPG) and graphene, the nature of the interaction between the modifying layer and the surface is less clear.

This presentation will describe our recent findings on aryldiazonium reduction at graphitic carbons. At glassy carbon, we have been expanding the protection-deprotection approach to circumvent the formation of multilayer films (Scheme 1B).[2] At HOPG, our scanning tunneling microscopy (STM), atomic force microscopy (AFM) and electrochemical studies have explored the importance of covalent bonding between the surface and modifiers.[3] Most recently, we have been using IR spectroscopy, AFM and electrochemistry to study aryldiazonium ion reduction and surface modification at graphene.



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### Role of carbon functionalization in oxygen reduction reaction

<u>Kateryna Artyushkova</u>, Alexey Serov and Plamen Atanassov University of New Mexico Chemical & Biological Engineering Department, Albuquerque, NM 87131 kartvush@unm.edu

Development and optimization of electrocatalysts framework is hindered by the complex nature of the materials, a partial understanding of the reaction mechanisms and precise chemistry of the active site or sites. The lack of this knowledge hinders the rational design of performance optimization strategies.

In Pt-based catalysis, carbon-based support is used to ensure electronic conductivity between the electrocatalyst and the current collector. Surface chemistry and structural morphology of support, catalyst and other components of catalyst layers are critical for mass transport properties, water and heat management and subsequently electrocatalytic activity and durability.

As an alternative to expensive Pt-based electrocatalysts, metal-nitrogen-carbon (MNC) and nitrogencarbon composites based on the graphene network have been studied extensively in recent years. There is still a partial understanding of the reaction mechanisms and precise chemistry of the active site or sites. There are two main hypotheses, one claiming that nitrogen functionalities on carbon-based support are directly responsible for their ORR activity and the second suggesting that nitrogen groups serve as the coordinating environment for metal where the ORR happens. Candidate structures participating in ORR consist of multitudes of nitrogen defect motifs in the carbon matrix of different degrees of graphitization with metal incorporated as metal particles as well as those linked to nitrogen defects in a variety of possible architectures.

In this report, the role of carbon functional groups in durability of Pt-based electrocatalysts and activity of MNC electrocatalysts is studied by multi-technique approach combining surface chemical analysis, morphological image processing and electrochemical testing.

Presented research combines the strength of several analytical and computational material sciences methods. Surface chemistry of individual building blocks will be characterized by XPS while morphology and roughness will be obtained by SEM and AFM. Correlation of structure and catalytic activity and durability of different families of electrocatalysts for oxygen reduction is achieved through the application of principal component analysis (PCA) to spectroscopic, macroscopic and microscopic data combined with results of electrochemical measurements on set of samples with range of electrochemical activities.

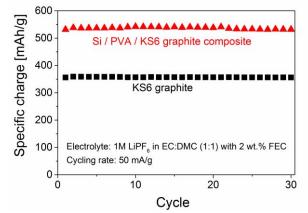
## Increasing the Life Time of Si/C Composite Electrodes for Lithium-Ion Batteries

Tiphaine Poux<sup>1</sup>, Juan Luis Gómez-Cámer<sup>1</sup>, Dario Cericola<sup>2</sup>, Thomas Hucke<sup>2</sup>, Michael E. Spahr<sup>2</sup>, Petr

<sup>1</sup>Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland <sup>2</sup>IMERYS Graphite & Carbon, CH-6743 Bodio, Switzerland tiphaine.poux@psi.ch

With the increasing energy demand, efficient energy storage and conversion systems are required. Lithium-ion batteries are among the most advanced storage systems and are highly used in mobile applications. Thanks to its low reaction potential and its impressive performance stability, graphite is the most common negative material for these batteries. However, its specific charge of 372 mAh/g is rather low for high energy applications. Today research is therefore focused on materials with higher specific charge to partially or totally replace graphite in negative electrodes. One promising candidate is silicon which displays a specific charge of 3579 mAh/g and whose reactions occur in a similar potential window than graphite. By simply mixing graphite with a small amount of silicon, high specific charge could already be obtained [1]. However, silicon-based electrodes suffer from strong performance fading upon cycling due to significant volume expansion and shrinkage of silicon during lithiation and delithiation processes. An advanced approach to increase the life time of the silicon-based electrodes is the milling of silicon with a carbon source followed by the carbonization of the carbon source [2]. Indeed, thanks to this route, silicon is well dispersed in a carbon matrix which can buffer the volume changes.

In this work, various carbon sources and carbonization conditions are used to tune the carbon matrix properties such as the morphology, dispersion or porosity, and *a fortiori* to play on the electrochemical performance of the composites. Each synthesized Si/C composite is characterized using X-Ray diffraction, thermogravimetric analysis, scanning electron microscopy combined with energy dispersive X-ray spectrometry, and gas adsorption techniques. Electrodes are then prepared using the composites as an additive to TIMREX® KS6 graphite and studied in half-cells using lithium counter electrode and constant current constant voltage technique. From these experiments, specific charge, coulombic efficiency, and cycling stability for several charge/discharge cycles are extracted. In order to understand the improved stability of the Si/C composites, ex-situ SEM and in-situ dilatometry studies are performed to investigate the morphology and volume changes, respectively. In addition to the influence of the carbon source and the carbonization conditions, the impact of the ballmilling conditions and of the electrode preparation is also investigated. High performance can already be obtained with polyvynil alcohol (PVA) as carbon source, addition of TIMREX® KS6 graphite during the ball milling step prior to the carbonization, and 5 wt.% of initial silicon content. Indeed, the specific charge of this electrode is very stable in FEC-containing electrolyte, and is ca. 45% higher that of graphite electrodes, which is highly promising for battery applications. The role of the FEC additive on the stability of the Si/C electrodes is also investigated in this work.



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Novák<sup>1</sup>

## Tin oxide/graphene nanocomposite as an effective electrode material for capacitive deionization technology

Khalil Abdelrazek Khalil<sup>1,\*</sup>, Ahmed G. El-Deen<sup>2</sup> and Nasser A. M. Barakat<sup>2, 3,\*</sup>

<sup>1</sup>Mechanical Engineering Department, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia
 <sup>2</sup>BioNanosystem Department, Chonbuk National University, Jeonju 561-756, South Korea
 <sup>3</sup>Organic Materials and Fiber Engineering Department, Chonbuk National University, Jeonju 561-756, South Korea
 <u>kabdelmawgoud@KSU.EDU.SA</u> (K. A. Khalil), Tel: +966502120039, Fax: +96614676652

and *nasser@jbnu.ac.kr* (N.A.M. Barakat)

Besides overcoming the water scarcity dilemma, brackish water desalination is required to avoid many diseases caused by the salty water including kidney failure, dehydration, hypertension and gastroenterology diseases. Desalination is a key technology to enhance both the quantity and quality of water[1]. Although there are several technologies have been introduced for water desalination such as multistage flash distillation (MSF), electrodialysis (ED) and reverse osmosis (RO), most of those methodologies need specialized and expensive infrastructures and require a great deal of energy and maintenance difficulties [2-5]. Capacitive deionization (CDI) is a second generation of electrosorption technique for removing the salt ions from the brackish water. Among the carbonaceous materials, graphene can be considered a promising CDI electrode due to its exceptional physical properties and chemical tenability if the specific capacitance could be improved. In this study, graphene/tin dioxide nanoparticles composites (Gr/SnO<sub>2</sub>) with different proportions were successfully synthesized via microwave irradiation; their electrosorption performances in CDI unit were investigated. The morphology, crystal structure and electrochemical performance were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and cyclic voltammetry. The obtained results indicated that incorporation of SnO<sub>2</sub> into graphene has a great impact for enhancing the electrosorption capacity. Compared to pristine graphene electrode, higher specific capacitance was observed for all the fabricated Gr/SnO<sub>2</sub> composite electrodes. Specifically, the electrode having 15 wt% SnO<sub>2</sub> exhibits distinguished electrochemical performances; high specific capacitance (323 F/g), excellent cycling stability, very good salt removal efficiency (83%), and distinct electrosorptive capacity of (1.49 mg/g). Overall, the present study demonstrates effective and facile route to distinctly improve the desalination performance of graphene-based electrodes for CDI technology.

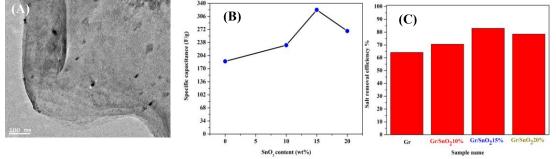


Fig. 1 TEM image for the introduced SnO<sub>2</sub>/graphene nanocomposite; (A), and influence of SnO<sub>2</sub> content on the specific capacitance; (B), and salt removal efficiency; (C).

#### Acknowledgment

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## CoNi-loaded graphene as effective non-precious electrocatalyst for methanol oxidation in alkaline medium

Nasser A. M. Barakat<sup>1,2,\*</sup>, Moaaed Motlak<sup>1</sup>, Mohammad Abdelkareem<sup>2</sup>, and Khalil Abdelrazek Khalil<sup>3</sup>

<sup>1</sup>BioNanosystem Department, Chonbuk National University, Jeonju 561-756, South Korea <sup>2</sup>Chemical Engineering Department, Minia University, El-Minia, Egypt <sup>3</sup>Mechanical Engineering Department, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

\*nasser@jbnu.ac.kr - Tel: 0082632702363 - Fax: 0082632704249

Depletion of the fossil energy sources forces the researchers worldwide to seek about convenient alternatives. Because of its simple system structure, low cost of fuels, and easiness of fuel handling compare to gas hydrogen, direct alcohol fuel cells (DAFCs) are very attractive electricity generating system [1]. Moreover, DAFCs have shown that they can produce higher current densities than proton exchange membrane fuel cells (PEMFCs) [2]. Among the introduced DAFCs, direct methanol fuel cells (DMFCs) have received much attention during the last decade [3], because methanol is an inexpensive, readily available, and easily stored and transported liquid fuel. The anodic reactions in the DMFCs are considered to be a combination of adsorption and electrochemical reaction on the anode surface [4]. Accordingly, because of the adsorption capacity, carbon has been incorporated in many recently reported electro-catalytic materials [5]. Graphene and alloy structure can overcome the main problem facing the non-precious electro-catalysts; low performance and poor stability. In this study, Co<sub>x</sub>Ni<sub>y</sub>-decorated graphene is introduced as novel, super effective and stable non-precious electro-catalyst for methanol oxidation. The obtained results have indicated that utilizing graphene as a support strongly enhances the electro-catalytic activity as the current density was doubled ten times, moreover a negative onset potential (-40 mV vs. Ag/AgCl) was obtained which is a distinct progress in the non-precious electro-catalysts research field. The electronic structure which is controlled by the alloy composition showed strong influence on the electro-catalytic activity;  $Co_0 Ni_{0,2}$  alloy nanoparticles revealed the best performance while Co<sub>0.1</sub>Ni<sub>0.3</sub> nanoparticles were the worst. Due to the alloy structure, the introduced graphenesupported electro-catalyst reveals distinguished stability. In-situ decoration of graphene by  $Co_x Ni_y$  alloy nanoparticle is utilized to produce the introduced electro-catalyst. Briefly, cobalt acetate and nickel acetate were added to the reaction media during graphene preparation using a modified chemical route. Later on, the resultant material was calcined in argon atmosphere at 850 °C.

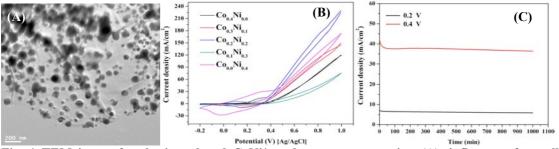


Fig. 1 TEM image for the introduced CoNi/graphene nanocomposite; (A), influence of metallic nanoparticle composition on the electroacatalytic activity; (B), and stability investigation; (C).

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## Onion-Like Nanocarbons and MXenes for Electrochemical Energy Storage Applications

<u>Vadym N. Mochalin</u>, Yury Gogotsi Department of Materials Science and Engineering, Drexel University, Philadelphia, PA 19104, USA <u>vadym@coe.drexel.edu; http://www.pages.drexel.edu/~vnm25/</u>

Nanomaterials hold tremendous potential in addressing some of the major challenges faced by our society, in particular, related to more efficient generation, storage and use of energy. Not only have nanomaterials played a role in specific energy related applications, they have revolutionized our approaches to solving these major societal challenges.

For example, the use of highly electrically conductive, small carbon nanoparticles with onion-like structure providing large surface and potential for ion intercalation<sup>1</sup>, allowed the design of conceptually novel supercapacitors, packing high power in a small size device, which can potentially revolutionize the area of microelectronics<sup>2</sup>. This makes it possible to design smaller cell phones, longer range RFID tags, implantable chips, smaller and higher power military nomad electronics, etc.

Another example is a quickly developing area of 2D materials for energy storage. The horizons of the 2D materials world, dominated until recently by graphene, have been significantly expanded with the discovery of the large family of novel 2D transition metal carbides/nitrides, named MXenes, in our lab in 2011<sup>3</sup>. The discovery of MXenes has added a few dozens of novel 2-D materials with tunable elemental composition, chemistry, and electronic properties to the current list<sup>4</sup>. Not surprisingly, this novel family of materials attracts increasing interest of research community, in particular, scientists working in energy storage<sup>5</sup>.

In this presentation, the synthesis of carbon nanoonions from detonation nanodiamond, as well as their structure, properties, and modifications for the use as electrode material in supercapacitors will be discussed. Recent studies on synthesis, properties, modeling, and potential applications of MXenes in Li ion batteries and supercapacitors, both carried out in our lab and published in literature will also be reviewed.

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## Electronic Properties and Morphological Characteristics of Carbon Nitride/Conjugated Polymer Composite Materials Aimed at Photocurrent Generation

Alain Pailleret<sup>1,2</sup>, Florence Billon<sup>1,2</sup>, Joshua C. Byers<sup>3</sup>, Claude Deslouis<sup>1,2</sup>, Oleg A. Semenikhin<sup>3</sup>

<sup>1</sup>Sorbonne Universités, UPMC Univ. Paris VI, UMR 8235, Labo. Interfaces et Systèmes Electrochimiques (LISE), 4, place Jussieu, case courrier 133, F-75005, Paris, France <sup>2</sup>CNRS, UMR 8235, LISE, F-75005, Paris, France <sup>3</sup>Department of Chemistry, The University of Western Ontario, London, Ontario, Canada

*E-mail* : *alain.pailleret@upmc.fr* 

Amorphous carbon nitride  $(a-CN_x)$  materials possessing a weak nitrogen content are high performance electronically conducting materials that have been widely investigated in view of applications in electrochemical treatment of liquid effluents, electrochemical sensors, catalysis, or anticorrosion coatings. On the other hand,  $a-CN_x$  materials can also behave as semi-conductors on condition that they possess the appropriate chemical composition [1], allowing them thus to be innovative candidates for the elaboration of new p-n junctions. This contribution is precisely aimed at tackling this issue. Interestingly, it also appeared in the course of our investigations that their amorphous character seems to be questionable as a function of the substrate they are deposited on.

In this contribution, carbon nitride thin films were deposited either onto indium tin oxide or onto electrogenerated poly(2,2'-bithiophene) (PBT, an electronically conducting polymer) substrates using a direct-current reactive magnetron cathodic sputtering technique, a graphite target and an  $Ar/N_2$  gas mixture [2,3]. The local morphology and electronic properties of the resulting thin films were investigated and compared using phase-imaging (PI-AFM) and current-sensing atomic force microscopy (CS-AFM). The semiconductor and photovoltaic properties of carbon nitride ( $CN_x$ ) thin films were investigated both individually and in composite materials resulting from their association with PBT.

The deposited materials were found to be generally amorphous with many individual nanostructured domains. The nature of the substrate was found to strongly influence the microscopic distribution of carbon nitride regions with the carbon nitride films showing some long-range order when deposited onto an undoped PBT substrate known to be much softer than ITO.  $CN_x$  films deposited on ITO using a low nitrogen content and a low deposition power (25-50 W) display a structure dominated by the abundance of the graphitic sp<sup>2</sup> regions. When they are deposited at higher nitrogen contents and magnetron power, CN<sub>x</sub> films started to demonstrate semiconductor properties, as evidenced by the occurrence of photoconductivity and the development of the space charge region. However, CN<sub>x</sub> films alone did not show any reproducible photovoltaic properties. However, CN<sub>x</sub> thin films lead to an efficient dedoping of n-doped PBT substrates they have been deposited on. Moreover, CN<sub>x</sub> thin films were found to function as acceptor materials, forming presumably a nanoscale bulk heterojunction (BHJ), when they are deposited on undoped PBT thin films. As a result, composite CN<sub>x</sub>/undoped PBT materials show improved photocurrent generation both in solution and in solid-state photovoltaic devices with the external quantum efficiencies reaching 1% at high nitrogen contents. The results suggest that carbon nitride materials may become a new promising family of materials in organic bulk heterojunction solar cells.

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## Chemically functionalized carbons for application in energy storage systems

Annaïg Le Comte<sup>1,2,3</sup>, Thierry Brousse<sup>2,3</sup>, <u>Daniel Bélanger<sup>1\*</sup></u> 1. Département de Chimie, Université du Québec à Montréal, CP 8888, succ. Centre-Ville

Montréal (Québec), Canada, H3C 3P8

2. Institut des Matériaux Jean Rouxel, UMR 6502 CNRS – Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 03, France.

3. Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France

\* belanger.daniel@uqam.ca

Electrochemical double layer capacitors are currently the subject of intense research worldwide due to the increasing use of such energy storage devices in a growing number of electrical/electronic systems. Carbon is currently the electrode material of choice for most practical devices due to its good capacitive behavior and performance and excellent chemical stability upon cycling. However, advances are needed to improve the energy density of carbon-based electrochemical capacitors.

In this presentation, we will present different approaches to modify carbon powder with electroactive quinones by using the diazonium chemistry (1,2). The resulting carbon modified with organic grafted groups will be used as active electrode materials in an electrochemical capacitor. The effect of various grafted groups on chemical, physical and electrochemical properties of the modified carbons will be discussed.

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## Carbon Nitrides: Multipurpose Materials for Electrochemical Applications

#### <sup>1,2</sup>C. Deslouis

#### <sup>1</sup>Sorbonne Universités, UPMC Univ. Paris VI, UMR 8235, Labo. Interfaces et Systèmes Electrochimiques (LISE), 4, place Jussieu, case courrier 133, F-75005, Paris, France. <sup>2</sup>CNRS, UMR 8235, LISE, F-75005, Paris, France. claude.deslouis@upmc.fr

Several carbon-based compounds emerged in the recent years to form a wide class of electroactive materials which present improved performances for electrochemical applications such as Boron-Doped Diamond (BDD), carbon nanotubes or graphene. Surprisingly, thin films of amorphous carbon nitrides, a-CNx, which show a wide potential window (> 3 V) in aqueous media and a significant reactivity with respect to outer sphere redox couples, have not been yet thoroughly investigated. As all these carbon materials, they are prone to a common sensitivity to the surface state and more generally to the history of the material with regards to the electrochemical reactivity. The dependence of the charge transfer resistance with the potential excursion applied to the electrodes allowed confirming for this class of materials the crucial role of pre treatments[1].

At variance with the drastic synthesis conditions for BDD, a-CNx films can be elaborated under milder conditions by cathodic sputtering in Ar-N<sub>2</sub> active plasma allowing the deposition of films on large areas. Therefore, not only the nitrogen content but also the surface chemistry due to a wide variety of chemical bonds or molecular orbitals between carbon and nitrogen can be tuned.

The already established properties of those materials will be detailed as illustrated by different techniques, namely XPS, SECM, CS-AFM, Raman Spectroscopy or EIS.

The nitrogen amount as precursor and the power of the various available preparation techniques (cathodic sputtering, filtered cathodic vacuum arc, laser ablation, ablation arc...) allow controlling not only the nitrogen content in the film but the chemical nature of the C-N bonds, the sp<sup>2</sup>/sp<sup>3</sup> ratio. These properties determine among others several characteristics as the electroactivity, the nature of the surface groups, the bulk electrical conductivity and the SC character.

-The wide potential window was at the origin of several applications like stripping analysis for heavy metals determination [2], also the control of the  $\zeta$  potential without interference of faradaïc reactions for electro-osmosis applications which require quasi-ideally polarizable surfaces [3] and show considerable improvement with the performance in separation with respect to the classical MIE configuration.

-The control of the surface chemistry combined with the wide potential window offered in electroanalysis comparable performances to BDD for example in the separation and determination of dopamine/ ascorbic acid [4].

-The n-type SC character of thin a-CNx films deposited onto conjugated poly-bithiophene substrate prepared with high nitrogen contents and power gives rise to photocurrent generation [5].

A survey of the already implemented applications based on these diverse properties is presented.

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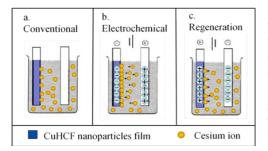
### Preparation and modification of 3-D nanostructure film of MHCF for electrochemical separation of Cesium

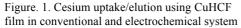
<u>R.Z. Chen</u><sup>a,b,</sup> Y.X. Zhang<sup>b</sup>, T, Kawamoto<sup>a</sup>, M. Asai<sup>a</sup>, C. Fukushima<sup>a</sup>, H. Tanaka<sup>a,\*</sup> a Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Japan

b University of Chinese Academy of Sciences, College of resources and environment, China crz0718@hotmail.com

#### Abstract

Transition metal hexacyanoferrates (MHCFs) are preferred to be competitive ion exchangers over other materials due to their selectivity and high capacity. In our previous study, a novel electrochemical column system using a nanoparticle film of copper (II) hexacyanoferrate (III) was proposed for selectively removing cesium. Multi-potential step (MPS) technique was conducted by stepping to + 1.0 V to load the film, and to + 0.5 V to unload the film. This process can be simply controlled by switching the potentials of CuHCFIII NPs film between +0.5 and +1.0V. The chemical equation was assumed as follow:  $Cu_3[Fe^{III}(CN)_6]_2$  (CuHCF<sup>III</sup>) +  $2e^- + 2Cs^+ \leftrightarrow Cs_2Cu_3[Fe^{II}(CN)_6]_2$ 





This system can be used for cesium separation without extra chemical reagents or any filtration treatment. Cesium uptake and elution can be simply controlled by switching the applied potentials between anodes and cathodes. The effective cesium removal with a high distribution coefficient can be adopted in a large pH range, and in the presence of several diverse coexisting alkaline cations, suggesting it can be taken as a promising technology for actual nuclear wastewater treatment [1,2]. The column system has been applied for long cycle experiment, results indicated well balance of Cs adsorption and desorption was achieved even after

100 cycles, which suggested a promising columns technology for sequential removal of Cs from actual nuclear wastewater.

However, such technology still cannot be applied for large scale utilization, due to the insufficient utilization of CuHCF film, or some other issue. For example, the low current efficiency of the film with a large surface, insufficient fills ratio of CuHCF nanoparticle, the passive reaction site on the electrode structure. According to theoretical calculation, only less than 25% of the Cs removal ability was found at the present state. Considering the huge amount of polluted Cs wastewater we facing, it is necessary to prepare and modify the nanostructure of MHCF film, and to enhance Cs separation performance.

As conductive filler, water-disperse of carbon nanotube (CNT) were mixed into the nanoparticle CuHCF ink, and then it can be uniformly coated on electrodes by simple wet process like conventional printing methods, so the column sizes and patterns are feasible at low cost. The fine conductive pass can be built among the unconnected CuHCF nanoparticle, which can reduce the electric resistance and result in an increase of the current efficiency. Furthermore, the nanostructure of CNT will fill the hollow or gaps existed in the simplex CuHCF film, this will also better the current efficiency, and then enhance the Cs separation performance.

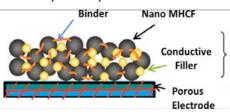


Figure. 2. Schematic of 3-D nanostructure film of MHCF and CNT

The objective of this study was to develop such 3D composited heterogeneous film nanoparticle film of CuHCF for Cs removal and to suggest a promising column technology for sequential removal of actual radiocesium wastewater.

Key words: Metal hexacyanoferrate complex, Electrochemical separation, Radioactive cesium, Carbon nanotube, 3-D nanostructure film

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## Inkjet Printed Carbon Nanotubes Electrodes for Environmental Sensing

#### Victor Costa Bassetto, Alexandra Bondarenko, Sunny Isaïe Maye, Fernando Cortés Salazar, Andreas Lesch, Hubert H. Girault<sup>#</sup> Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland <sup>#</sup> hubert.girault@epfl.ch

The quantification of a wide range of analytes in environmental and biological samples by means of amperometry shows many advantages in terms of rapidness, reliability and low cost. Moreover, electrochemical strategies can easily be miniaturized, multiplexed and integrated into lab-on-a-chip devices. Such electrochemical systems are generally fabricated by photolithography, screen-printing and, more recently, by inkjet printing (IJP) techniques. Indeed, IJP continuously gains more interest, since it enables the digital and mask-less deposition of functional inks containing e.g. metallic nanoparticles, biomolecules or polymers, that can be treated almost simultaneously by thermal or photochemical post-processing techniques,<sup>1-3</sup> on a wide range of materials.

Carbon nanotubes (CNTs) as electrode materials have demonstrated several beneficial properties in respect to catalysis, kinetics, stability, conductivity and, particularly interesting for fabrication purposes, printability.<sup>4</sup> Herein, we present reproducible stand-alone CNT electrodes on flexible materials by the IJP of commercial and self made CNT inks. The final fully inkjet printed sensors are composed of electric circuits, the stand alone CNT working electrodes, counter and reference electrodes and on top an insulation layer to define accurately the active electrode areas and to protect the underlying electric circuits. We give an overview of our applied printing strategies of carbon based materials using different IJP systems with separated and integrated post-processing techniques, such as photonic curing. Single and multiplexed (*e.g.* 16 integrated electrochemical cells) sensors have successfully been fabricated and applied for the monitoring of micropollutants (*i.e.* atrazine) in aqueous samples applying magnetic beadbased immunoassays.

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## Effect of Anodic and Cathodic Pretreatment on the Electrochemical Activity of Boron-Doped Diamond Electrodes from Different Sources

<u>Kallyni Irikura</u><sup>1\*</sup>, Orlando Fatibello Filho<sup>1</sup>, Romeu C. Rocha-Filho<sup>1</sup> and Greg M. Swain<sup>2</sup> <sup>1</sup> Department of Chemistry – Federal University of São Carlos, São Carlos, SP, Brazil <sup>2</sup> Department of Chemistry – Michigan State University, East Lansing, MI, USA

\* kallyni@gmail.com

It is well known that sp<sup>2</sup> carbon electrodes generally require some form of pretreatment to activate the surface prior to use. The degree of activation imparted by a particular pretreatment depends on the pretreatment conditions and the microstructure of the carbon electrode. Far less is understood about activating boron-doped diamond electrodes, which often do not require activation for optimum performance. However when they do, solvent cleaning and electrochemical pretreatment have been shown to be effective. As highlighted by Suffredini et al. [1], the predominant surface termination on boron-doped diamond (BDD) electrodes can be changed by proper selection of the electrochemical pretreatment conditions. Anodic pretreatments (AP) increase the carbon-oxygen functional group coverage making the surface hydrophilic, whereas cathodic pretreatments (CP) favor hydrogen termination rendering the surface more hydrophobic [2]. This is important to recognize because the electrochemical activity of BDD electrodes for some redox species is strongly affected by the surface termination [2,3]. In this work, we investigated how AP and CP affect the electrochemical activity of BDD electrodes from two sources. We used 1,1'-dimethyl-4,4'-bipyridinium dichloride, commonly known as methyl viologen (MV) or paraquat, as a redox probe. MV has three main oxidation states: MV<sup>2</sup>  $\Rightarrow$  MV<sup>+</sup>  $\Rightarrow$  MV<sup>0</sup>. Due to its favorable redox properties, MV has been electrochemically investigated on different electrode materials such as glassy carbon, gold, mercury, and BDD [4-6]. Polycrystalline BDD electrodes were purchased from NeoCoat, Switzerland (Si substrate, 1.2 cm × 1.2 cm and B doping of 10,000 ppm) and Fraunhofer CCL USA (Nb substrate, 1.2 cm × 1.2 cm and B doping of 6000-8000 ppm). A 20 mL electrochemical cell was used with a BDD (~ 0.33 cm<sup>2</sup>) working electrode, a Pt counter electrode, and an Ag/AgCl (3M KCl) reference electrode. AP or CP was performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> by applying 10 mA cm<sup>-2</sup> for 10 s or -160 mA cm<sup>-2</sup> for 480 s, respectively. Cyclic voltammetry was performed with the as-received, AP- and CP-treated BDD electrodes at different scan rates (50-500 mV  $s^{-1}$ ) from -0.2 to -1.3 V. By comparing the cyclic voltammograms (CVs) obtained at 150 mV  $s^{-1}$  for the electrodes in the blank solution (1 M KCl), it was clear that after CP the cathodic background current decreased for the NeoCoat electrode (by about 15%, at -1.0 V. e.g.), but increased markedly (by about 130%) for the Fraunhofer electrode, which thus showed a higher activity for the hydrogen evolution reaction. The CVs obtained for 0.1 mM MV presented the usual two pairs of redox peaks, one at -0.71 and -0.65 V, which is associated with the redox reaction represented in eq. 1, and another at -1.02 and -0.97 V, associated with the redox reaction involving the neutral molecule (see eq. 2).

 $MV^{2+} + e^- \Rightarrow MV^+$  (1)  $MV^+ + e^- \Rightarrow MV^0$  (2) However, the anodic peak currents obtained after both AP and CP were smaller than those obtained using as-received electrodes, while the  $\Delta E_p$  values remained constant ( $\leq 60 \text{ mV}$ ); hence, the electrochemical pretreatment of the electrodes decreased their activity for MV oxidation. On the other hand, the plots associated to a Randles-Sevcik analysis of the anodic peak currents for both electrodes, after AP and CP, clearly showed that these anodic peak currents had a linear dependence on the square root of the scan rate; thus, we could conclude that both oxidation processes are controlled by diffusion, in agreement with previous studies [3]. In summary, the electrochemical pretreatments affected the electrochemical activity of the two BDD electrodes. Further experiments are underway, using other redox species, aiming at understanding the obtained results.

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## The Influence of the Electrolyte pH on the Mechanism of Electrodegradation of Estrone in a Flow Reactor Using a Boron-Doped Diamond Anode

Ricardo F. Brocenschi<sup>a</sup>\*, Bianca F. da Silva<sup>b</sup>, Romeu C. Rocha-Filho<sup>a</sup>, Nerilso Bocchi<sup>a</sup>, Sonia R. Biaggio<sup>a</sup>

<sup>a</sup> Department of Chemistry, Universidade Federal de São Carlos, São Carlos – SP, Brazil <sup>b</sup> Institute of Chemistry, Universidade Estadual Paulista, Araraquara – SP, Brazil \*ricardo.fbro@gmail.com

Nowadays, water quality is one of the most important topics in environmental chemistry. Furthermore, considerable attention has been focused in one class of organic pollutants, the so-called endocrine disrupting compounds (EDCs). Estrone (E1) is an EDC that has been frequently detected in wastewater. Due to the increased awareness of the risks involved in the E1 toxicology, public health officials have been wondering and analyzing whether usual treatment processes effectively remove this chemical from water and wastewater. In this sense, electrochemical technology may be an alternative to remove these organic compounds from wastewater, being a low-cost, simple, rapid, and clean approach to the removal of many organic pollutants in water and wastewater. The oxidation of organics may be carried out by hydroxyl radicals (OH) electrogenerated by water oxidation (oxygen evolution reaction – OER) and the oxidation power of specific anodes depends on the interaction between 'OH and the electrode surface [1]. Taking these concepts into account, in this study we evaluated the effect of the electrolyte pH (3, 7, and 10) on the nature of the intermediate compounds formed during the electrolysis of estrone using a boron-doped diamond (BDD) electrode. Aqueous 500 µg L<sup>-1</sup> E1 solutions (V = 500 mL) in 0.1 M Na<sub>2</sub>SO<sub>4</sub> were electrolyzed in a flow reactor  $(q_V = 2 \text{ Lmin}^{-1})$  as previously described by Aquino *et al.* [2], with a stainless-steel cathode. The electrodegradation kinetics was followed by UV-Vis spectroscopy and the influence of the electrolyte pH on the degradation pathway was investigated using mass spectroscopy (MS or MS/MS - negative mode). Solidphase extraction was used to increase the E1 concentration and eliminate any electrolyte before injecting the sample in the mass spectrometer. The kinetics of intermediates formation during the electrolysis was assessed through the area of the extracted-ion chromatogram (XIC) before starting the electrolysis  $(t_0)$  and after the following electrolysis times: 5, 10, 20, 30, 40, and 50 min. The E1 degradation pathway was also comparatively investigated using a  $\beta$ -PbO<sub>2</sub> anode. Initially, the total ion chromatogram (TIC) was obtained monitoring m/z 100 – 450 for the electrolyte at pH 3, and E1 was detected with at a retention time (t<sub>r</sub>) of 11.16 min. Additionally, the TIC showed that many other bands were present, but all these bands were also present in the blank (without E1 in solution), indicating that these interferents were present in the matrix. These bands were always compared for the TICs of E1 solution and blank; thus, it was possible to eliminate any false positive result. After that, all detected ions were fragmented by MS/MS and a fragmentation pathway was proposed. The intermediates detected during the electrolysis at pH 3 were  $[M-H]^- m/z$  269 (E1), 285, 303 ( $t_r =$ 8.2 and 9.7 min), 349, 397, 399, and 357. Some of these intermediates were also detected at pH 7, but in reduced number ( $[M-H]^-$  m/z 269, 285, 349, 359, 333, and 375). When the electrolyte pH was 10, the number of detected intermediates was considerably reduced; all but one of them were also detected at pH 3 and 7 ( $[M-H]^-$  m/z 269, 285, 349, 333); the new intermediate was detected with  $[M-H]^-$  m/z 317. Thereby, from these results, it is clear that the pH has a strong influence, both in species and number, on the degradation pathway during the estrone oxidation process using the BDD electrode as anode, with pathway degradations that are similar just in the initial step. The oxidation power of the BDD electrode led to excellent results in the oxidation of E1 (98% vs. 35% for the  $\beta$ -PbO<sub>2</sub> electrode). Furthermore, there is significant influence of the two anode materials on the obtained intermediate products (just three common intermediates were detected:  $[M-H]^{-}$  m/z 269, 285, 349) and, consequently, on the proposed E1 degradation pathways.

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## Nanocomposite of Polyaniline and Multiwalled Carbon Nanotubes for Use as Optical and Electrochemical Sensor

<u>Fábio S. Lisboa</u>, Marcio Bergamini, Luiz H. Marcolino Jr., Aldo J. G. Zarbin Department of Chemistry, Universidade Federal do Paraná (UFPR) Av. Cel. Francisco Heráclito dos Santos, 210, Jardim das Américas, CEP 81531-990, Curitiba-PR, Brazil lisboa.silva.fabio@gmail.com

Nanocomposites formed by the interaction between conductive polymers and carbon nanotubes (CNT) have been widely studied and applied in different technical fields, for example, electrochromic materials, photovoltaic devices, sensors and the development of supercapacitors, because of the properties caused by the interaction of these two classes in nanocomposite materials.<sup>[1]</sup> Among the most used polymers is polyaniline (PANI), which has some advantages compared to other conductive polymers, such as high conductivity in its protonated form (emeraldine salt), with values that can reach about of  $10^3$  S cm<sup>-1</sup> Besides the conductivity, different oxidation states can be obtained on the redox processes and the low cost of its monomer are other factors that makes the polyaniline a product of great interest for the development of projects in the above areas.<sup>[2]</sup> The interaction between the polymer with carbon nanotubes gives an increase of the electrical properties and thermal stability to the nanocomposite. For the construction of an electrochemical sensor which operates also as optical, two characteristics of materials to be synthesized are extremely important: the conductivity and transparency. Thus, to obtain the nanocomposite PANI/CNT on the thin film form is a very attractive alternative because it contemplates the main requirements mentioned above, however, the low solubility of polyaniline hinders the formation of thin films of this polymer, but the interfacial synthesis route developed by our research group minimizes this problem because the stabilization of particles in liquid-liquid interface allows the formation of homogeneous and stable thin film. In this work will be discussed the preliminary studies of the electrochemical behavior of nanocomposite thin films formed by the interaction between polyaniline and multiwalled carbon nanotubes at a mass ratio of 16: 1 (PANI: CNT) deposited on tin oxide doped with indium substrates (ITO). Cyclic voltammetry studies were carried out for various films using ascorbic acid as a probe molecule, in order to verify the electrochemical behavior of these nanocomposites. The oxidation potential for ascorbic acid changes to lower values when PANI/CNT is used in comparation with ITO, indicating an electrocatalityc process. The nanocomposite also presented good sensibility, due the increase in current is given when aliquots of ascorbic acid are added to de medium. The results for the preliminary studies qualify the PANI/CNT as a promising material for the development of electrochemical sensors.

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## Production of Electrolytic Manganese Dioxide on Boron-Doped Diamond for Use in Lithium Batteries

Rogério A. Davoglio<sup>\*</sup>, Sonia R. Biaggio, Romeu C. Rocha-Filho, Nerilso Bocchi Department of Chemistry - Federal University of São Carlos C.P.676 – 13565-905 São Carlos, SP – Brazil, phone 55(16)33518210 \* rogeriodavoglio@gmail.com

In recent years, the use of rechargeable batteries has become essential in everyday life in modern society. This is mainly due to their use in portable devices or as a source of propulsive electric power for cars. However, to meet the needs of this new demand for energy, cathode materials, with better performance, lower cost and toxicity began to be developed. Among the different materials studied by several research groups, LiMn<sub>2</sub>O<sub>4</sub> with a tridimensional structure that facilitates the intercalation of lithium ions emerges as one of the most promising candidates as cathode material for these batteries. Therefore, the aims of this study were to investigate the possibility of producing electrolytic manganese dioxide (EMD) on borondoped diamond (BDD) and subsequently convert it to the  $LiMn_2O_4$  spinel by microwave-assisted solidstate reaction. EMD was obtained using an aqueous 1 mol  $L^{-1}$  MnSO<sub>4</sub> + 0.3 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> solution<sup>[1]</sup> at room temperature and current densities of 0.1, 1.0, and 5.0 mA cm<sup>-2</sup>, with current efficiencies of approximately 99, 70, and 62%, respectively. This decrease in the current efficiency for the production of EMD at higher current densities is due to the favoring of the  $O_2$  evolution reaction. In addition, a morphological change of the EMD was observed with increasing applied current densities, obtaining small needle-like fibers at 0.1 mA cm<sup>-2</sup>, rods at 1 mA cm<sup>-2</sup>, and globular particles at 5 mA cm<sup>-2</sup>. By analyzing theses samples using X-ray diffraction (XRD), we found that all diffractogram peaks are in agreement with the crystallographic form for the  $\varepsilon$ -MnO<sub>2</sub> phase (JCPDS 30-0820 card). However, from the ratio between the first and second diffraction peaks, it was possible to identify a small amount of  $\gamma$ -MnO<sub>2</sub> phase (JCPDS-39-0375), which decreases with increasing current density. The predominance of the  $\varepsilon$ -MnO<sub>2</sub> phase is an important feature because it has ideal interstitial characteristics for conversion into the spinel with a high degree of inclusion of lithium ions, compared to other phases of  $MnO_2^{[2]}$ . After the characterization of the EMD obtained samples, its conversion into LiMn<sub>2</sub>O<sub>4</sub> spinel was performed by reacting ε-MnO<sub>2</sub> and LiOH.H<sub>2</sub>O at a ratio 1:2 under microwave irradiation for 3 min. XRD analyses of the material so obtained indicated that the  $LiMn_2O_4$  spinel was obtained with a cubic structure (JCPDS 35-0732 card) after only 3 min of irradiation. Furthermore, these diffraction patterns presented intense and well-defined peaks, characteristic of materials with high crystallinity, a factor that favors the electrochemical processes of insertion of  $L_1^+$  ions into the LiMn<sub>2</sub>O<sub>4</sub> structure. Next, the electrochemical behavior of the obtained LiMn<sub>2</sub>O<sub>2</sub> spinel was investigated. Voltammetric profiles (obtained in a 1 mol  $L^{-1}$ LiClO<sub>4</sub> EC / DMC solution at  $0.1 \text{ mV s}^{-1}$ ) exhibited all the characteristic peaks of this spinel, being a clear indication of the efficiency of the solid-state synthesis used to convert DME into the LiMn<sub>2</sub>O<sub>4</sub> spinel. On the other hand, galvanostatic charge-discharge tests in a three-electrode cell configuration yielded specific-capacity values of 94, 91, 88, 85, and 82 mA h  $g^{-1}$  when obtained at discharge rates of C/5, C/4, C/3, C/2, and C/1, respectively. Therefore, we could conclude that it was possible to produce  $\varepsilon$ - $MnO_2$  (with different morphologies, depending on the current density used), which was successfully converted into the LiMn<sub>2</sub>O<sub>4</sub> spinel by a microwave-assisted solid-state reaction; furthermore, this spinel presented adequate electrochemical properties. Finally, it is also noteworthy that the significantly reduced time needed for the microwave-assisted solid-state synthesis of the spinel may lead to energy savings of approximately 90% when compared to the conventional thermal synthesis<sup>[3]</sup>.

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## Direct and Indirect Electrochemical Degradation of Tebuthiuron Using a Boron-Doped Diamond Anode in a Flow System

Gabriel F. Pereira, <u>Nerilso Bocchi</u><sup>\*</sup>, Bianca F. da Silva, Regina V. Oliveira, Sonia R. Biaggio, Romeu C. Rocha-Filho Department of Chemistry, São Carlos Federal University C.P. 676, 13560-970, São Carlos - SP, Brazil <sup>\*</sup>bocchi@ufscar.br

Tebuthiuron (TBH) is a herbicide widely used in sugarcane cultivation. However, it is highly toxic, according to ANVISA (National Agency for Sanitary Vigilance of Brazil). On the other hand, Muneer et al. 2005 [1] pointed out that the greatest sources of herbicides in the environment are industrial effluents. In this context, the study of technologies for treating effluents containing TBH molecules is relevant. Among these, electrochemical technology has been shown effective for removing various organic molecules, in many cases presenting high efficiency and good versatility. To study the electrochemical degradation of TBH, 1.0 L of an aqueous solution containing this compound (100 mg L<sup>-1</sup> from a commercial formulation of 500 g  $L^{-1}$ ) and 0.1 mol  $L^{-1}$  Na<sub>2</sub>SO<sub>4</sub> (supporting electrolyte) was prepared in the presence or absence of 25 mmol  $L^{-1}$  NaCl. A flow system (6.5 L min<sup>-1</sup>) with a boron-doped diamond anode (BDD 2000 - 4500 ppm from Condias, Germany; 36.4 cm<sup>2</sup>) and stainless steel (AISI 304) cathodes was used. The effect of current density in the presence and absence of Cl<sup>-</sup> ions was investigated; the degradation process was monitored by high-efficiency liquid chromatography (HPLC), and chemical oxygen demand (COD) and total organic carbon (TOC) content determinations. Liquid chromatographymass spectrometry (LC-MS) was also used to identify degradation intermediates; for such, electrolyses of an aqueous 100 mg  $L^{-1}$  TBH solution prepared from an analytical standard were carried out. The obtained results showed that the removal rate of TBH increased with the current density in the absence of CΓ. No change in COD was observed, indicating that a mass transport limitation was achieved in the process. For the two highest values of current density, a similar behavior was verified for COT removal. With the addition of  $C\Gamma$  ions to the solution, no effect on the removal rate of TBH and TOC was observed, indicating that active-chlorine species were not able to oxidize the TBH molecules. However, a dramatic decrease in COD occurs, indicating a possible formation of organochlorine species (not detected by oxidation with dichromate ions) from the reaction between degradation intermediates and active-chlorine species. From the LC/MS measurements, several reaction intermediates were detected (see Table 1). As can be seen in these data, the formation of organochlorine compounds (in red) was detected when the electrolysis was carried out in the presence of Cl<sup>-</sup> ions, evidencing their hole in the COD reduction.

Compound	<b>Retention time / min</b>	Molecular ion / ( <i>m</i> /z)	Ionic fragments / ( <i>m</i> / <i>z</i> )
		No NaCl	
1	4.38	215	158
2	2.45	245	214, 188, 156, 101, 74
3	2.94	245	188, 156, 146, 132, 86, 57
4	3.40	245	215, 172
5	7.95	243	215,172, 116
		$[NaCl] = 25 \text{ mmol } L^{-1}$	
1	4.39	206	157, 142
2	4.38	215	158
3	2.12	245	188, 170
4	2.81	172	116, 89
5	8.26	263	206, 157, 142

**Table 1:** Degradation intermediates detected during the electrochemical oxidation of an aqueous 100 mg  $L^{-1}$  TBH solution using a BDD anode in a flow system (6.5 L min<sup>-1</sup>).

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### Electroreduction of nitrate using diamond films and different cathodes

Vilma Araújo da Costa<sup>1,\*</sup>, Danyelle M. de Araújo<sup>2</sup>, Sibele B. C. Pergher<sup>1,2</sup>, Carlos A. Martínez-Huitle<sup>2</sup>

<sup>1</sup>Federal University of Rio Grande do Norte, Science and Engineering of Materials Department, Campus Universitario – Lagoa Nova, Natal RN, Brazil.

<sup>2</sup> Federal University of Rio Grande do Norte, Instituto de Química, Lagoa Nova CEP 59078-970 - Natal, RN, Brazil

Email: vilmacostabio@gmail.com

Nitrates in water result mainly from the organic pollution caused by urban agglomerations. However, other important nitrate-sources are fertilizers used in agriculture, discharges from certain industries, as well as some combustion processes. Typically, wastewater undergoes a complex series of mechanical, physical, chemical and biological treatments, which point at the elimination of pollutants for the subsequent restitution of purified water to the environment or for reutilization. While anions that form insoluble compounds are removable by precipitation, nitrates are water-soluble and their abatement from aqueous media requires specific approaches. The electrochemical approach may in fact represent a quite effective de-polluting way, which adds the electric parameter to the usual chemical variables and, exploiting it, the ability to inject energy into the system, modifying the stability of reagents and products, as well as that of any other transient species [1,2]. In this frame, we propose the use of electrochemical technology as alternative to remove nitrates from water in order to eliminate their strong ecotoxicological consequences. Then, the principal objective of this study is to collect several samples of drinking and potable waters for quantifying the nitrates concentration. This work investigated the effect on the use of different cathodic materials (Cu, Ti/Pt, graphite and boron-doped diamond (BDD)) for the electrochemical reduction of nitrate. Several applied currents were investigated (0.1, 0.2, 0.5 and 1.0 A) on the removal of nitrates from aqueous solutions in undivided electrochemical cell (250 mL) equipped with conductive diamond film as anode. Results clearly demonstrated that the elimination of nitrate was partially removed from synthetic solutions after 3 h of electrolysis, achieving 88%, 68%, 58% and 30% when Cu, Ti/Pt, graphite and BDD electrodes were used as cathodes, respectively; under better experimental conditions. However, in some cases, production of nitrite was attained, principally when BDD electrodes were used in the electrochemical cell. Conversely, the elimination of nitrate and byproducts (nitrite and N-derivates) was more efficiently performed when a Cu-cathode material was used. This behavior is due to the high electrocatalytic surface of Cu material than at BDD cathode [2]. Ti/Pt and graphite were no efficient cathodic materials to remove nitrate from synthetic solutions. Nitrate ion species are considered environmental pollutants in quantities above the recommended limit, which can lead to serious environmental and health. Therefore, the applicability of electrochemical reduction approach was tested by elimination of nitrate from real samples of drinking water polluted with NO<sub>3</sub>, obtaining important results.

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# Electrochemical detection of copper using glassy carbon electrodes modified with multiwalled carbon nanotubes

P. Jara-Ulloa, S. Catalán-Caro

Department of Chemistry, Faculty of Sciences, University Andrés Bello (UNAB)

Av. República # 275, Santiago, Chile.

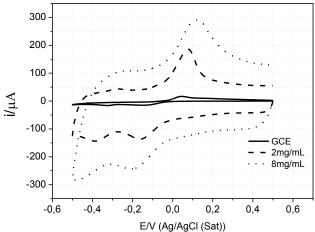
paola.jara@unab.cl

In recent years we have studied the use of multiwalled carbon nanotubes (MWCNTs) as electrode surface modifiers, this due to the unique properties of this material presents, such as its electrical capacity, chemical, mechanical and structural.

On the other hand, copper is an important material in the industry, its importance grows up constantly for instance, because of the electronic devices such as, laptops and cell phones in which copper is the main element of the modern electronic circuits. These copper circuits are generally made by electroplating, based on *aqueous solutions* that contain *copper ions* which are potentially pollutants. For this reason, developing a simple method to detect  $Cu^{2+}$  on aqueous samples becomes tremendously important and interesting.

A three-electrode system was used for all measurements. A glassy carbon electrode (GCE) with a diameter of 3 mm was used as the working electrode and platinum wire as the auxiliary electrode. All measurements were carried out with an reference Ag/AgCl electrode. Electrochemical measurements were recorded on electrochemical analizer CH Instruments 620D.

Before each modification, the GCE was cleaned by polishing alumina, and then was washed with abundant water. The MWCNT were dispersed at different concentrations (mg mL-1) with water by sonication for 5 min. The sonication



procedure was repeated three times. The Immobilizing the carbon nanotubes are made by casting the GCE with 5  $\mu$ l of the dispersion of carbon nanotubes.

The modified GCE electrode was immersed in a stirred supporting buffer solution containing  $Cu^{2+}$ , the accumulation time was variable and no potential was applied during this step.

Using the optimal accumulation time found (8 min), reproducibility and repeatability studies were performed, The CNTs/GCE were very reproducible but little repeatable, thus to perform a calibration curve was necessary to use a different electrode for each concentration measured.

The use of electrochemical analysis tool, specifically for obtaining modified electrodes with CNTs offer an alternative for determining the presence of  $Cu^{2+}$  ions by optimizing parameters of modification and testing alternatives to these would be possible in the future to achieve its application in the treatment of wastewater.

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## Triclosan Detection on a Molecularly Imprinted Carbon Nanotube Sensor

Josimar Aquino de Araújo, Thaylan Pinheiro Araújo, <u>Ilanna Campelo Lopes</u>, Sônia Maria Carvalho Neiva Tanaka, Iranaldo Santos da Silva, Auro Atsushi Tanaka Universidade Federal do Maranhão - Centro de Ciências Exatas e Tecnologia Avenida dos Portugueses, 1966 – Bacanga, 65080-805 São Luís (MA), Brasil ilannacampelo@hotmail.com

Electrochemical sensors are important tools in the medical, biological, and environmental fields. The incorporation of highly selective recognition elements in these devices can improve sensitivity and specificity. A promising technique for specific molecular recognition is the use of molecularly imprinted polymers, involving the polymerization of functionalized monomers in the presence of a removable template molecule. This work describes the development of a hybrid material based on carbon nanotubes (CNT) and a molecularly imprinted polymer (MIP), as an electrochemical sensor for sensitive and selective detection of triclosan (TCN), 5chloro-2-(2,4-dichlorophenoxy)phenol, one of the most prevalent antibacterial compounds found in products. The electrode modification consisted of using a sol-gel process to structure molecularly imprinted siloxane (MIS) on a glassy carbon electrode (GCE) previously modified with a film formed from chitosan and carbon nanotubes (CCNT). Characterization of the new GC/CCNT/MIS sensor by cyclic voltammetry indicated that the binding sites formed on the electrode surface by removal of the template (triclosan) increased the sensitivity of the system, as analyte oxidation was facilitated. The results also showed that the sol-gel process with alkaline catalysis substantially enhanced the response of the sensor to TCN. The analytical curve was linear in the concentration range between  $3.98 \times 10^{-6}$  and  $3.85 \times 10^{-5}$  mol L<sup>-1</sup>, and limits of detection (LOD) and quantification (LOQ) were 1.40 x  $10^{-6}$  mol L<sup>-1</sup> (0.41 x  $10^{-3}$  g L<sup>-1</sup>) and 4.67 x  $10^{-6}$  mol L<sup>-1</sup> (1.35 x  $10^{-3}$  g L<sup>-1</sup>), respectively.

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## Electrochemical effect of chloride on the oxygen evolution reaction and its application as alternative for treating an effluent using platinum and diamond anodes

Dayanne Chianca de Moura, Camila Carvalho de Almeida, Mariana de Oliveira Medeiros, Maria Jucilene de Macedo Melo, Carlos Alberto Martínez-Huitle

*Federal University of Rio Grande do Norte, Institute of Chemistry Lagoa Nova - CEP 59.072-970, RN, Brazil. Phone/Fax: +55 (84) 3215-3825.* 

E-mail: dayannechianca@gmail.com

The day-to-day human and industrial activities have influenced the flow and storage of water and the quality of available fresh water. Physical-chemical methods, chemical oxidation, and advanced oxidation processes (AOP) are currently used to treat effluents [1,2]. In this context, oxidative electrochemical technologies offer an alternative solution to several environmental problems regarding the wastewater treatment, because electrons provide a versatile, efficient, cost-effective, easily automation, and clean reagent [2]. Some years ago, the effective application of electrochemical technologies for the treatment of organic pollutants has been relatively small. But nowadays, thanks to intensive investigations that have improved the electrocatalytic activity and stability of electrode materials and optimized reactor geometry, electrochemical technologies have reached a promising state of development and can be effectively used for disinfection and purification of wastewater polluted with organic compounds [3,4]. The most used types of electrode for this electrochemical approach are the metal oxide electrodes that, generally, are the derivatives of four metal oxides, SnO<sub>2</sub>, PbO<sub>2</sub>, RuO<sub>2</sub>, and IrO<sub>2</sub>. However, Ti/Pt and BDD anodes are also able to produce appreciable amounts of reactive oxygen species and other oxidizing species such as active chlorine [5], peroxodisulfate, peroxodicarbonate and peroxodiphosphate coming from the oxidation of ions present in the solution, also allowing a fast and permanent disinfection. In this work, the role of chloride respect to the oxygen evolution reaction by using BDD and Ti/Pt anodes was investigated to understand the performance of both anodes for the electrochemical treatment of a real sample of wastewater, with lower organic load, generated at Federal University of Rio Grande do Norte. Bulk experiments were performed under real discharged effluent conditions (pH and conductivity) in order to verify the applicability of direct and mediated oxidation by applying 2.5 and 5.0 mA cm<sup>-2</sup>. Results clearly showed that, a partial elimination of chemical oxygen demand (COD) was achieved, depending on applied current density. Using Ti/Pt, by applying 2.5 and 5.0 mA cm<sup>-2</sup>, COD removal efficiencies of 25.2% and 30.49% were obtained. Under the same conditions, a minor COD removal was achieved by using BDD electrode. However, the removal efficiencies were improved when mediated oxidation approach was employed, obtaining 63.7% and 60% for Ti/Pt by applying 2.5 and 5.0 mA cm<sup>-2</sup>, respectively; while for BDD electrode COD removals were about 15% and 47%, under the same conditions. These figures are in agreement with the polarization curves obtained, where it was possible to confirm that the concentration of halide in solution increases the importance of Cl<sub>2</sub>/oxy-chloro radicals system depending on the electrocatalytic material and this behavior plays an important role in relation with the oxygen evolution reaction, influencing on the efficiency of electrochemical apporach adopted. Other DDB electrodes with configurations different sp<sup>3</sup>-sp<sup>2</sup> (diamond-graphite) are being tested in order to verify the influence of the relationship  $sp^3-sp^2$ .

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## Ultrasensitive Simultaneous Determination of Dihydroxybenzenes Isomers at Ultrathin Film Based On Hybrid Material SiO<sub>2</sub>/MWCNT Decorated With Ag Nanoparticles

Paulo A. Raymundo-Pereira, Thiago C. Canevari, Sergio A. S. Machado Instituto de Química de São Carlos, Universidade de São Paulo, PO Box 780, 13560-970 São Carlos, SP, Brazil pauloaugustoraymundopereira@gmail.com

Synthesis, characterization, and applications of a mesoporous silica/multiwalled carbon nanotube (SiO<sub>2</sub>/MWCNT) hybrid material obtained by a sol–gel process and decorated with silver nanoparticles (AgNPs) ranging in size from 5 to 8 nm were described in this study. The AgNPs were prepared directly on the surface of the SiO<sub>2</sub>/MWCNTs material by using N,N-dimethylformamide (DMF) as the reducing agent, and the resulting material was designated Ag/SiO<sub>2</sub>/MWCNT. The Ag/SiO<sub>2</sub>/MWCNT material was characterized by scanning electron microscopy (SEM - Fig. 1), energy-dispersive X-ray spectroscopy (EDS - Fig. 1), high-resolution transmission electron microscopy (HR-TEM - Fig.2), and X-ray photoelectron spectroscopy (XPS).

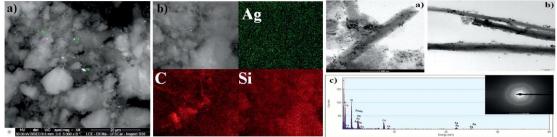


Fig. 1 – SEM images of Ag/SiO<sub>2</sub>/MWCNT hybrid material (a) and EDS Fig. 2 – HR–TEM micrographs of hybrid (a), (b) and EDX spectrum (c).

A glassy carbon electrode modified with the Ag/SiO<sub>2</sub>/MWCNT hybrid material was used in the development of a sensitive electrochemical sensor for the determination of hydroquinone and catechol in the presence of resorcinol by square wave voltammetry. Well-defined and separate oxidation peaks were observed in phosphate buffer solution (PBS) at pH 7.0 (Fig. 3 (a)). The Ag/SiO<sub>2</sub>/MWCNT/GC exhibited high sensitivity for the simultaneous determination of hydroquinone (HQ) and catechol (CAT) in the presence of resorcinol (RES), and the limits of detection for hydroquinone and catechol were 0.0117 and 0.0121  $\mu$ mol L<sup>-1</sup>, respectively, Fig. 3 (b). No significant interference was observed for 2,6-dichloroindophenol, phenol, 4-nitrophenol, and nitrite ions in the detection of dihydroxybenzenes.

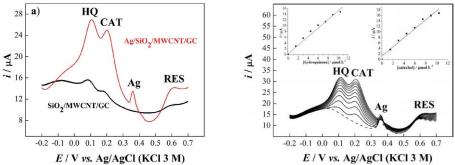


Fig. 3 – Square wave voltammograms of HQ, CAT and RES at  $GC/SiO_2/MWCNT/Ag$  and  $GC/SiO_2/MWCNT$  (a). Simultaneous determination of HQ and CAT in the presence of 2.0 x 10<sup>-5</sup> mol L<sup>-1</sup> RES (b). Inset: analytical curves.

Our study demonstrates that the resultant  $Ag/SiO_2/MWCNT/GC$  can be used for hydroquinone and catechol detection in the presence of resorcinol and other potentially interfering materials in river water samples. Acknowledgments to FAPESP (2012/17689-9 and 2013/17053-0) by financial support.

# Understanding the production of persulfate using boron-doped diamond (BDD) electrode

Karla C. de Freitas Araújo<sup>1</sup>, Danyelle M. de Araújo<sup>1</sup>, Mariana O. Medeiros<sup>1</sup>, Hamilton Varela<sup>2</sup>, Djalma R. da Silva<sup>1</sup>, Carlos A. Martínez-Huitle<sup>1,\*</sup>. <sup>1</sup>Universidade Federal do Rio Grande do Norte, Instituto de Química, RN, Brasil.

<sup>2</sup> Instituto de Química de São Carlos da Universidade de São Paulo, Brasil

carolaraujo.ufrn@vahoo.com.br

Between the various oxidants available, persulfate  $(S_2O_8^{-2})$  has been notable in recent years for use in soil remediation and decontamination of effluents. As studies to reduce levels of pollution have intensified in recent times it has become important to find a more efficient way of producing persulfate, as it has been increasingly used in oxidation processes in situ [1]. The electrode of boron-doped diamond (BDD) has attracted considerable interest of researchers due to its excellent properties for electroanalysis [2], non-active nature and its power to produce hydroxyl radicals (BDD('OH)) from water discharge on its surface from reaction (physically adsorbed on the anode surface;  $H_2O \rightarrow {}^{\bullet}OH + e^{-} + H^{+}$ ). In the case of the sulfuric acid in aqueous solution can promote the formation of persulfate via two mechanisms [3-4].

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$$
(1)  
2HSO\_4^{-} \rightarrow S\_2O\_8^{2-} 2H^+ + 2e^- (2)

However, some authors have suggested that reactions between  $^{\circ}$ OH radicals and sulphate, already present in solution, produce persulfate (S<sub>2</sub>O<sub>8</sub><sup>-2</sup>) [3-4]. However, no attempts have confirmed this electrochemical way because the studies are frequently performed at diluted sulfuric acid solutions. Thus, the object of this work was to study the effect of the ratio H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub> on the electrochemical behavior of surface at BDD anode in order to verify the possible participation of hydroxyl radical on the production of persulfate at different temperatures (313 K and 333 K). Cyclic voltammetry studies and polarization curves were performed to understand the electrochemical behavior of BDD surface when different concentrations of H<sub>2</sub>O were added to H<sub>2</sub>SO<sub>4</sub> concentrated.

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## Carbon-Based Electrodes Modified with Ionic Liquids for Drug Analysis

<u>A. Álvarez-Lueje</u>, B. Pérez, P. Pizarro, V. Moncada Faculty of Chemical and Pharmaceutical Sciences, Department of Pharmacological and Toxicological Chemistry, University of Chile Sergio Livingstone Pohlhammer 1007, Santiago, Chile aalvarez@cig.uchile.cl

In this work, the development of two types of carbon-modified electrodes used for the analysis of drugs is presented. The first type corresponds to glassy carbon electrodes modified with carbon nanotubes and different ionic liquids (GCE-IL) and second, to carbon paste electrodes modified ionic liquids (CPE-IL). Both types of electrodes were modified with ILs of three types: a) alkyl-type: ethyldimethyl-propylammonium bis (trifluoromethylsulfonyl) imide (IL-1) and ethyldimethyl (2-methoxyethyl) ammonium tris (pentafluoroethyl) trifluorophosphate (IL-2), b) imidazole-type: 1-butyl-3-methylimidazolium hexafluorophosphate (IL-3) and 1-butyl-3-methyl-imidazole tetrafluoroborate (IL-4), c) pyridinium-type: N-butyl-3-methylpyridinium trifluoromethanesulfonate (IL-5), N-butyl-3-methyl pyridinium hexafluorophosphate (IL-6) and N-butyl-4-methylpyridinium tetrafluoroborate (IL -7).

The electrochemical characterization of the different modified electrodes was carried out with the redox mediator potassium ferricyanide, ferrocenemethanol and hexaamineruthenium (III) chloride, using cyclic voltammetry. Each IL was tested at different percentages (5% - 15% w/w), exhibiting a significant increase in the anodic and cathodic currents of each mediator in all the modified electrodes studied, depending on the percentage of IL tested.

Different carbon-based modified electrodes with ILs were selected for both the study of the electrochemical behavior and the development of analytical methods for the quantification of different drugs by differential pulse voltammetry in Britton Robinson buffer solution. Thus, the cathodic behavior drug nimesulide (GCE-CNT-IL-5) and the anodic behavior of pseudoephedrine (GCE-CNT-IL-3), chlorpheniramine (GCE-CNT-IL-3), methyldopa (GCE-CNT-IL-5), levodopa (CPE-IL-3) and benserazide (GCE-CNT-IL-3) was studied, and by using differential pulse voltammetry, methods of quantification for each drug were also developed, determining the corresponding parameters of analytical efficiency. As example, the parameters obtained for nimesulide, methyldopa and levodopa are summarized in the following table:

Parameter	Nimesulide	Methyldopa	Levodopa
Repeatability, %CV	4.6	3.5	2.4
Reproducibility, %CV	5.6	4.3	4.8
Calibration curve (I <sub>p</sub> , μA)	$I_p = 0.0265 \times C (ng/mL) - 0.597 (r^2=0.997)$	$I_p = 0.0259 \times C (ng/mL) + 0.211 (r^2 = 0.992)$	$I_{p} = 0.236 \times C (\mu g/mL) - 0.559 (r^{2} = 0.999)$
Linear range	30-1233 ng/mL	21-2110 ng/mL	6-30 μg/mL
LOD (ng/mL)	16.6	6.9	1800
LOQ (ng/mL)	23.6	7.4	4100
Experimental conditions	$pH = 10, E_{app.} = -0.3 V,$ acc. time = 5 min	pH = 2, acc. time = 4 min	$pH = 2, E_{app.} = 0.3 V,$ acc. time = 4 min

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# Electrochemical properties of boron doped diamond electrodes with low and high diamond content

Jéssica Pires de Paiva Barreto<sup>1</sup>, Elisama Vieira dos Santos<sup>1</sup>, Manuel A. Rodrigo<sup>2</sup>, Djalma R. da Silva<sup>1</sup>, Carlos A. Martínez-Huitle<sup>1,\*</sup>

<sup>1</sup> Institute of Chemistry, Federal University of Rio Grande do Norte, Campus Universitario, Lagoa Nova, Natal, RN, Brazil.
<sup>2</sup>Department of Chemical Engineering, Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain mhuitle@hotmail.com

Recent studies have proved that the electrochemical efficiency of boron doped diamond (BDD) is strongly related to the relation of  $sp^3/sp^2$  ratio during anodic oxidation, favoring an active or non-active surface nature [1,2]. However, a part of this behavior is due to the electrochemical properties of diamond electrodes, such as potential window, oxygen evolution reaction at higher potentials, electron-transfer rate and so on. This characterization can give the information about the choice of a specific BDD electrode to particular electrochemical application. However, these assumptions were not completely verified because no electrochemical characterization has been performed for BDD anodes with significant differences on the  $sp^3/sp^2$  ratio. Thus, the aim of this work was to present important evidences about the influence of diamond content on BDD surface on their electrochemical features.

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### Method validations for high performance liquid chromatography and

### U/Vis to study intermediates compounds of phenol eletrooxidation

### using boron doped ultrananocrystalline diamonds films

<u>M. Santos</u><sup>1,2\*</sup>, A.F. Azevedo<sup>2</sup>, M.R. Baldan<sup>2</sup>, N.G. Ferreira<sup>2</sup> *Fatec Pindamonhangaba – Pindamonhangaba – SP - Brasil* <sup>2</sup>*INPE/LAS, São José dos Campos – SP – Brasil* 

1,2\* marta.santos4@fatec.sp.gov.br

Different papers that reporting the electrooxidation of phenolic compounds do not take into account the necessity of analytical criteria associated to the high performance liquid cromatography (HPLC) measurements or UV is analysis of the compounds formed during the process, i.e., no method validation is presented. Thus, the objective of this work was to develop and validate a HPLC method and study UV is analysis of the intermediates compounds for phenol oxidation using boron doped ultrananocrystalline diamonds films. The electrodes were deposited on silicon substrates using a HFCVD reactor in a gas mixture of  $CH_4/H_2/Ar$  (01/19/80 sccm) for 16 h, 900 K and 6.7 kPa. The boron doping was obtained using an additional H<sub>2</sub> line passing through a bubbler containing B<sub>2</sub>O<sub>3</sub> dissolved in methanol. Phenol and the intermediate compounds such as hydroquinone, *p*-benzoquinone, cathecol, fumaric acid, maleic acid, and oxalic acid were selected to develop this HPLC method as well as the UV is analysis. The validated method was used for kinetic studies of this eletrooxidation processes.

## Synthesis and Characterization of PAni/CNT/CF Composites: morphological, structural and electrochemical analyses

D.A.L. Almeida, M. C. D. Oliveira, C. P Fonseca, M.R. Baldan, N.G. Ferreira Instituto Nacional de Pesquisas Espaciais, INPE São José dos Campos, SP, CEP 12227 010 dalva.dri@gmail.com

Conducting polymer represents a class of important material called as "synthetic metals" due to their electric, electronic, magnetic and optical properties inherent to metals or semiconductors. Among the conducting polymers, polyaniline (PAni) has attracted much attention because of their environmental stability, controllable electrical conductivity, and easy processability. However, it has some disadvantages for practical application, such as low stability during cycling due to changes in volume during the process of charge/ discharge. To reduce this effect, several authors used a matrix, which serves as a template for the growth of the polymer. In this case, carbonaceous materials such as carbon nanotubes (CNT), carbon fiber (CF) among others, have proven to be excellent materials to orient the polymer chains during the synthesis process [1]. Most of these studies deal with the polymerization of PAni with carbon nanotubes (single- and multiwalled) and nanofibres [2, 3] and there are various papers reporting the synthesis of PANI-carbon composites with carbon materials such as cloths, graphene sheets, fibers, and powdered activated carbon [4]. The composites made of PAni and carbon nanotubes (CNTs) represent a bunch of interesting materials because the capacitive behavior of carbon materials can be further improved by the presence of active species as conducting polymer, which contribute to higher performance of the composite. The objective of this work is the production and the characterization of ternary PAni/CNT/CF composite using the commercial multiwalled NTC Aldrich. Particularly, these composites were obtained by growing PAni on CF immersed in the solution containing NTC previously dispersed and functionalized in the reaction medium. The composites were produced at three deposition times of 30, 60 and 90 min. They were characterized by scanning electron microscopy (SEM), Raman scattering spectroscopy, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The electrochemical analyses were made by cyclic voltammetry and charge/discharge tests. The composite PAni/CNT/CF showed the tubular morphology, where the PAni also worked as a binder between the CF and CNTs. The PAni contained at the composites is found under form of emeraldine salt (ES) according to the band characteristic present in the Raman spectra, such as in the region 1340 cm<sup>-1</sup>, 1336 cm<sup>-1</sup>, 1481 cm<sup>-1</sup> and 1610 cm<sup>-1</sup>. In the tests of the charge and discharge, the curves are symmetrical and the capacitance values around 500 F g-1 was observed. Besides, It was observed from cyclic voltammetry, that the composites present characteristic peaks from the redox process of polyaniline, as well as a capacitive profile, that shows the viability of application of this material as electrodes to supercapacitors.

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# Evaluation of BDDE surface pre-treatment towards the oxidation of indolic compounds

Caroline S. Gomes, Rafael M. Buoro, Othon S. Campos, Silvia H. P. Serrano

Laboratório de Bioeletroquímica, Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo Av. Prof. Lineu Prestes, 747, B2 S,- sala 273, 05508-000, São Paulo, SP, Brasil sanz.gomes@gmail.com

Boron-doped diamond (BDD) is often used as an electrode material because of its attractive properties, such as chemical and electrochemical stability, as well as high conductivity due to the presence of a charge carrier within its crystallographic structure. In addition, BDD electrodes (BDDE) can be used in a large potential window in aqueous solution and present lower background current than other carbon-based electrodes, allowing certain specific electrochemical reactions in high potential values. BDDE pre-treatments can modify the functional groups of their surface, aiming improved conductivity and selectivity [1,2]. The aim of this work was to evaluate BDDE pre-treatments towards the oxidation of indolic compounds, such as tryptophan, an essential aminoacid. The oxidation of tryptophan ( $E_{pa} = 0.83V$ ) occured in lower positive potentials when cathodic pre-treatment (c-BDDE) was applied in comparison to anodic pre-treatment ( $E_{pa} = 0.85V$ ) (a-BDDE) or thermal pre-treatment in oxidizing atmosphere ( $E_{pa} = 0.90V$ ) (air-BDDE). The hydrogen terminations of c-BDDE possibly improve the adsorption kinetics of tryptophan onto the BDDE surface due to the hydrophobic aspect of the indol electroactive group. Other indol derivatives, such as indol and serotonin will be further evaluated.

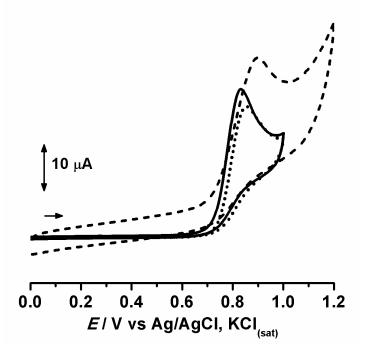


Figure 1 - Cyclic voltammogram obtained of 100µM tryptophan in ph 7.0 phosphate buffer solution 0,1M for — cathodic pre-treatment, ••• anodic pre-treatment and — — thermal pre-treatment.

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# The effect of multi-walled carbon nanotube dimensions on the electrochemical oxidation of phenolic compounds

Rafael M. Cardoso, <u>Eduardo S. Almeida</u>, Rodrigo H. O. Montes, Rafael M. Dornellas, Edson Nossol, Eduardo M. Richter, Rodrigo A. A. Muñoz\* *Instituto de Química, Universidade Federal de Uberlândia (UFU), Uberlândia-MG, Brazil* 

raamunoz@iqufu.ufu.br

The electrochemical oxidation of phenolic compounds at functionalized multi-walled carbon nanotubes (MWCNTs) modified electrodes was investigated in function of MWCNTs of different dimensions, namely large diameter MWCNT (LD-MWCNT) and small diameter MWCNT (SD-MWCNT) corresponding to the dimensions of 100–170 nm x 5–9  $\mu$ m and 6–9 nm x 5  $\mu$ m (D x L), respectively. An aliquot of 10 µL of dispersions of 1 mg/mL in dimethylformamide of functionalized MWCNTs was applied to a bare glassy-carbon electrode (1.5 mm diameter). Cyclic voltammetry of hydroquinone (HQ), catechol (CT), tert-butyl hydroquinone (TBHQ), 2,6-di-tert-butyl-4-methylphenol (BHT) and 2,6-di-tertbutyl-phenol (TBP) was performed at the unmodified and MWCNT-modified surfaces using 0.1 mol  $L^{-1}$ HClO<sub>4</sub> as electrolyte. The electrochemical response for all phenolic compounds at MWCNT modified GCE presented short decrease in the overpotential of the oxidation reactions (< 100 mV). However, the values of  $\Delta E$  ( $E_{anod}-E_{cath}$ ) for the electrochemical oxidation of HQ, CT, and TBHQ at unmodified GCE were 0.24, 0.24 and 0.26 V, respectively, and were considerably reduced to 0.13, 0.16 and 0.20 V at the LD-MWCNT surface and to 0.09, 0.08 and 0.04 V at the SD-MWCNT modified GCE, which indicated the higher electrocatalytic activity of SD-MWCNT. Additionally, a substantial increase (3-fold) in the current for the oxidation of HO and TBHO at SD-MWCNT modified GCE was obtained while the same was not verified for the oxidation of the other phenolic compounds studied in this work. The phenolic group in BHT and TBP molecules is strongly impeded by steric hindrance, which also explains the more positive potentials required for the oxidation of BHT and TBP (~0.9 V vs. Ag/AgCl) even at unmodified GCE in comparison with HQ, CT and TBHQ (0.5 to 0.6 V vs. Ag/AgCl). The modification of the GCE surface with MWCNTs did not improve the electron transfer of the oxidation of BHT and TBP. Raman spectroscopy analysis revealed that SD-MWCNT presented high degree of structural defects based on the higher D/G ratio value in comparison with LD-MWCNT. X-ray diffraction (XRD) patterns of both materials indicated absence of metallic impurities and higher number of structural defects in the SD-MWCNT (based on  $d_{002}$ ). Therefore, these analyses corroborated the higher electrocatalytic activity of SD-MWCNT for the electrochemical oxidation of phenolic compounds.

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## Comparative Studies on Impact of Immobilization Method on Direct Electron Transfer of Glucose Oxidase Adsorbed on 4-(pyrrole-1-yl) Benzoic Acid Modified Carbon Nanotubes

<u>Katarzyna Jakubow</u>, Barbara Kowalewska Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland k.jakubow@student.uw.edu.pl

In our research we constructed glucose bioelectrocatalytic systems by the immobilization of glucose oxidase enzyme (GOx) onto a multi-walled carbon nanotubes (MWCNTs) modified glassy carbon electrode. MWCNTs have extraordinary mechanical, electronic, thermal, and structural properties [1]. Modification of MWCNTs with 4-(pyrrole-1-yl) benzoic acid (PyBA) improves effective transfer of electrons between the active center of the enzyme molecule (GOx) and the electrode surface. The presence of PyBA in composite system significantly improves their stability and facilitates immobilization process by introduced new functional carboxylic groups [2].

The main goal of our research was to compare two different enzyme immobilization methods to construct bioelectrocatalytic systems: i.e., covalent immobilization using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride and crosslinking with glutaraldehyde. Cyclic voltammetry and amperometry were utilized for characterization of the MWCNTs/PyBA-GOx systems. Both systems containing carbon nanotubes and glucose oxidase exhibit a pair of well-defined reversible redox peaks. CNTs/PyBA-GOx exhibits a typical surface-controlled process at the fabricated electrode surface involved two-electron and two-proton. Both of our carbon nanostructure electroactive protein systems are capable of effective oxidation of glucose in neutral buffer solution. Immobilization method had the influence on all electrochemical parameters, for example: the apparent Michaelis–Menten constant, sensitivity, electron transfer rate constant ( $k_s$ ) and limit of detection. The system based on covalent enzyme immobilization showed a sensitivity of 20.0  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> and K<sub>M</sub>=14.7 mM. But the system based on protein crosslinking displayed higher sensitivity of 28.0  $\mu$ A mM<sup>-1</sup> cm<sup>-2</sup> and lower K<sub>M</sub>=10.2 mM. The difference in the bioelectrocatalytic system response can be attributed to protein conformational or dynamical changes during covalent immobilization. Physically immobilized enzyme was characterized by greater stability and activity compared with the enzyme immobilized by the chemical method. However, both systems provide a promising platform for the development of biofuel cells and biosensors.

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## Ethanol Sensing and Direct Electrochemistry of Adsorbed Alcohol Oxidase on 4-(pyrrole-1-yl) Benzoic Acid Functionalized Carbon Nanotubes

<u>Katarzyna Jakubow</u>, Barbara Kowalewska Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland k.jakubow@student.uw.edu.pl

Alcohol oxidase (AOx) (EC 1.1.3.13) as bio-recognition element for ethanol sensing has stimulated interest during the last years. AOx belongs to oxidoreductases, it is oligomeric enzyme consisting of eight identical subunits each containing a tightly bound flavin adenine dinucleotide (FAD) redox center. This enzyme molecule is used to catalyze the oxidation of short-chain, primary aliphatic alcohols to their respective aldehydes [1]. To facilitate electron transfer between enzyme molecule and electrode surface we utilized multi-walled carbon nanotubes (MWCNTs). They are extremely attractive for wide range of sensing applications from structural materials because of their unique mechanical and electronic properties [2]. The main goal was to combine these two elements leading to formation of the integrated bio-electrocatalytic system for effective oxidation of ethanol.

Our research is based on direct electron transfer (DET) of alcohol oxidase immobilized onto multi-walled carbon nanotubes modified with 4-(pyrrole-1-yl) benzoic acid (PyBA). It is reasonable to expect that functional carboxylate groups from PyBA form stable covalent amide linkages with amine groups from the enzyme molecule, which significantly improves stability of our integrated system [3]. DET facilitated by the modified MWCNTs/PyBA between the AOx protein and the glassy carbon electrode was confirmed. The immobilized enzyme displayed a pair of well-defined and reversible redox peaks. The formal potential taken by potential values of the  $E_a$  and  $E_c$  in scan rate 25 mV/s was -0.454 V vs. Ag/AgCl in 0.1 M phosphate buffer solution pH=7.0. The apparent Michaelis-Menten constant was calculated by the electrochemical version of the Lineweaver-Burk plot and was found to be  $K_M$ =36.2 mM. Moreover, MWCNTs/PyBA-AOx system was found to exclude interference caused by the common electroactive species such as ascorbic acid, uric acid and glucose. The findings of the investigation have established the direct electrochemistry of the AOx protein and its potential biosensor application for quantitative detection of alcohol in real samples.

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## Electrochemical Oxidation as an Alternative to Remove Dyes from Textile Effluent using Pt and carbon electrodes

<u>Maiara Barbosa Ferreira</u><sup>1</sup>, Aline Maria Sales Solano<sup>1</sup>, José Heriberto Oliveira do Nascimento<sup>2</sup>, Djalma Ribeiro da Silva<sup>1</sup>, Carlos Alberto Martinez Huitle<sup>1</sup>

 <sup>1</sup>Federal University of Rio Grande do Norte, Institute of Chemistry Lagoa Nova - CEP 59.072-970, RN, Brazil. Phone/Fax: +55 (84) 3215-3228.
 <sup>2</sup>Federal University of Rio Grande do Norte, Department of Textile Engineering, Lagoa Nova - CEP 59.072-970, RN, Brazil.
 E-mail: mahbarbosaferreira@hotmail.com

Disposal of textile effluents without previous treatment has been a major problem that relates to visual and environmental pollution, since synthetic organic dyes are highly toxic and difficult to degrade. Synthetic dyes are highly colored and formulated to resist to chemical, biochemical and photochemical changes. The textile industry also uses an average of 10,000 different dyes and pigments and the environmental problem is augmented by estimates that up to 50.000 tons of wastewater is discharged into rivers and streams worldwide [1]. The electrochemical treatment is one of methods for removing organic and inorganic impurities from water and wastewater. Consequently, several research groups are trying to use electrochemical methods as an effective alternative for detoxification of wastewaters containing biodegradable pollutants. As an innovative alternative, the electrochemical processes have been proposed recently for treating wastewater containing dyes [2, 3]. This study aimed to apply the electrochemical technology for treating a textile effluent containing three different dyes using an electrochemical flow reactor (EFR) by applying 30 and 60 mA/cm<sup>2</sup>. The effluent was obtained at laboratory scale by using trichromatic reactive dyeing from cotton fabric. The residual dyeing baths were subjected to an electrochemical treatment and reused in a second dyeing process. As the nature of the anode material influences strongly both the selectivity and efficiency of the EO process was used and equipped with Pt and Carbone anode. Then, elimination of dye solution was performed using EFR and the results demonstrated that the electrochemical oxidation is quite satisfactory in removing textile pollutants due to its low operating costs, easy handling and efficient elimination of the intensity of color and their ecotoxicological effects.

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## Photoelectrolyses of Rhodamine B in Chloride Media

Danyelle Medeiros de Araújo<sup>1</sup>, Cristina Sáez<sup>2</sup>, Pablo Cañizares<sup>2</sup>, Carlos Alberto Martínez-Huitle<sup>1\*</sup>,

Manuel Andrés Rodrigo Rodrigo<sup>2</sup>

<sup>1</sup> Federal University of Rio Grande do Norte, Instituto de Química, Lagoa Nova CEP 59078-970 - Natal, RN, Brazil;<sup>2</sup>Department of Chemical Engineering. Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain.

danyelle.quimica@yahoo.com.br

In the recent years, the electrochemical treatment of dyes has demanded an attention special, focused mainly on the comparison of different anode materials [1-4] or technologies (photoelectro-Fenton and photoelectrocatalysis) [4-5], to the removal of particular dyes and the feasibility of the electrochemical technology in the remove these dyes. The electrochemical treatment by direct or indirect approaches, is based on the elimination of pollutants directly on the anode surface, via production of OH or/and other oxidants, such as chlorine, (per)bromate, persulfate, ozone, hydrogen peroxide, percarbonate, and others, directly on-site using only water, salt, and energy. In the case of active chlorine, the interest in this oxidant is based on the ubiquitous presence of chloride ions in a certain number of effluents and natural waters, making possible the involvement of active chlorine during electrochemical treatment; and the chemistry and electrochemistry of higher oxidation states for chlorine close to neutral pH [4-6]. In this work, the role of chloro-species generated during the electrolysis of Rhodamine B solutions containing chloride and perchlorate salts as supporting electrolytes is studied. Likewise, the effect of light irradiation in the activation of the oxidants is also evaluated. To do this, essays of electrolysis, photoelectrolysis and chemical oxidation in presence of light with the oxidant generated electrochemically were carried out. Results show that Rhodamine B was effectively oxidized by electroirradiated techniques. Color removal is faster than Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) removal, due to the rapid attack of chromophore group of the molecule. In general, light irradiation has a positive effect during the electrolysis of RhB at high current densities. In chloride media, light irradiation seems to favour the decomposition of hypochlorite. Effect of light irradiation is explained in terms of the activation of oxidants in the bulk of the electrolytic treatment by production of highly efficient radicals. Results of chemical oxidation essays may indicate that UV light irradiation has not a clear catalytic influence out of an electrolytic environment.

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# Catalytic activity towards H<sub>2</sub>O<sub>2</sub> reduction of carbon composites containing MFe<sub>2</sub>O<sub>4</sub> nanoparticles.

<u>Fabiana A. Gutiérrez</u><sup>1</sup>, Eva. Mazario<sup>2</sup>, M. Dolores Rubianes<sup>1</sup>, Gustavo A. Rivas<sup>1</sup>, Pilar Herrasti<sup>2</sup>, Soledad Bollo<sup>3,4</sup>, José H. Zagal<sup>5</sup>, F. Javier Recio<sup>5</sup>

<sup>1</sup>INFIQC (UNC-CONICET), Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, X5000GYA Córdoba, Argentina.

<sup>2</sup>Faculatd de Ciencias Químicas, Departamento de Química Física Aplicada, Universidad Autónoma Madrid, España

<sup>3</sup>Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile. <sup>4</sup>Advanced Center for Chronic Diseases (ACCDiS). Universidad de Chile.

<sup>5</sup>Facultad de Química y Biología, Departamento de Química de los Materiales, Universidad de Santiago de Chile. Chile

Among magnetic oxides, magnetite nanoparticles supported on graphite powder have well-established catalytic properties for many reactions such as decomposition of alcohols, selective oxidation of carbon monoxide, decomposition of hydrogen peroxide and discoloration of synthetic dyes, and have been extensively studied for environmental applications and biosensors [1, 2]. The integration of nanoparticles (NPs) and carbon nanomaterials as supported material in nanocomposites has recently become a hot topic of research due to their new and/or enhanced functionalities that cannot be achieved by either component alone, and therefore holds great promise for a wide variety of applications in catalysis, biomedical fields, drug delivery, energy storage and removal of contaminants from wastewater.

The present work inform a systematic study of the effect of different carbon supported nanomaterials (nanotubes and graphene) on the catalytic activity of three kinds of MFe<sub>2</sub>O<sub>4</sub> nanoparticles (M = Mn, Co, Fe) at pH 13. Nanostructured ferrites were electrochemically synthesized according to ref. 3, and stabilized with citrate. X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersed spectroscopy (EDS) were used for chemical and structural characterization. The ferrite nanoparticles shown a similar size (20 nm) and shape. The dispersions were obtained by mixing Np and carbon nanomaterials in mass ratio (1:4) with 5 mL of a mixture of water, isopropanol and nafion, followed by sonication for 30 min. Before modification, the GCEs were polished with alumina slurries of 1.0, 0.30, and 0.05  $\mu$ m for 2 min each. After that, they were modified by dropping 10  $\mu$ L of the given dispersion on the top of the surfaces followed by the evaporation of the solvent.

The modified electrodes were evaluated by Scanning Electrochemical Microscopy (SECM), Cyclic voltammetry (CV), Amperometry and Electrochemical Impedance Spectroscopy (EIS). Electrochemical characterization experiments were performed at de-oxygenated pH 13 solution (NaOH 0.1M) at room temperature. The catalytic activity of the nanocomposites was performed by cathodic polarization at 5mV/s in presence of 10 mM H<sub>2</sub>O<sub>2</sub> and evaluated by their onset potential. The sensitivity was determined as the slope of the calibration plots obtained from the amperometric recordings. The charge transfer resistance ( $R_{ct}$ ), associated with the electrocatalytic activity of the nanoparticles, was obtained of the EIS

The catalytic activity of nanoparticles are higher than nanotubes or graphene evaluated independently, following the next sequence (Mn>Co>Fe). However, a clear decrease of the onset potential is detected when both kind of nanocomposites (MWNT-NP and GORT-NT) with different nanoparticles are evaluated. The higher analytical sensitivity and and lower  $R_{tc}$  of nanoparticles was detected when Co or Mn and MWNT were used follow by Fe. The best synergic effect of the C nanocomposites are evaluated taking into account the relative increase of sensitivity and the decrease in  $R_{ct}$  respect the bare Np. In the case of the use of graphene a similar increase of 1.5 times are detected independent of the Nanoparticle tested. However the effect of nanotubes is dependent of the cation with an increased of 6, 2.8 and 1.8 for Fe, Mn and Co respectively.

In conclusion, the use of ferrite-C nanocomposites have shown a clear increase in the catalytic activity and sensitivity of bare nanoparticles, the synergic effect of the C materials if higher when CNT are used and is dependent of the chemical composition of the nanoparticles.

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## Electrochemical Degradation of Phthalates Using Boron Doped Diamond Electrode

Rodrigo del Río<sup>1,2</sup>, F. Armijo<sup>1,2</sup>, María José Rubio<sup>1</sup>, Daniel Correa<sup>1</sup>, Camila Araneda<sup>1</sup>

<sup>1</sup>Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile <sup>2</sup>Centro de Nanatecnología y Materiales Avanzados CIEN-UC, Pontificia Universidad Católica de Chile Vicuña Mackenna 4860, Macul, Santiago, Chile

e-mail address: rdelrioq@uc.cl

Phthalates or phthalic acid esters (PAEs) are among the most widespread environmental contaminants worldwide. Some phthalates are developmental and reproductive toxicants in rats especially affecting the male reproductive apparatus [1]. These phthalates are a class of organic compounds used as additives in plastic manufacture, namely, polyvinyl chloride (PVC), polyvinyl acetates, cellulose and polyurethanes. Phthalates are difficult to degrade in conventional way; here is where the electrochemical oxidation using boron doped diamond (BDD) and others anodes are applied with interesting results, due to their versatile electrocatalytic property of active chlorine electrogeneration, electrochemical stability, and long lifetime [2].

In this Work we compare the degradation of diethyl and dimethyl phtahlates (DEP and DMP) using a BDD electrode in a filter-press cell. Typical conditions of the electrolysis were: 100 ppm of the phthalates in a 0.05 M Na<sub>2</sub>SO<sub>4</sub> electrolyte with or without 0.05 M NaCl at 5.5 L min<sup>-1</sup>. The current density used varied between 10 mA cm<sup>-2</sup> to 30 mA cm<sup>-2</sup>. The degradation of the organic compounds was followed by TOC, COD, UV-Vis spectra and HPLC. Figure 1 A shows that the presence of the chloride anion in the electrolyte have not effect in the degradation of DEP, indicating that the phtahlates have a oxidation potential higher than the potential of the chloride or active chlorine species. On the other hand, BDD has a bigger oxidant power than others anodes commonly used in degradation studies, and this fact was confirmed comparing with DSA and PbO<sub>2</sub>, where the BDD degraded more efficiently DEP and DMP than the other ones (figure 1 B). Figure 1C, shows the HPLC chromatograms registered as function of time, showing that the DEP are decaying as the electrolysis takes place and more hydrophilic compound start to appear. After 4 hours of degradation the DEP concentration decreases until 10 % approximately. Same experiments with DMP show similar behavior (data not shown). In conclusion, DEP and DMP could be degraded using BDD anode but the presence of Chloride in the electrolytic media has not effect.

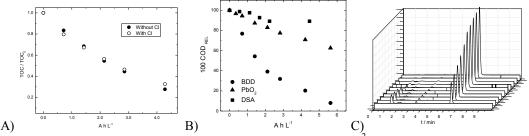


Figure 1 a) TOC decay in the degradation of DEP in 0.05 M  $Na^2SO_4$  with and without 0.05 M NaCl, current density 30 mA cm<sup>-2</sup>, 5.5 L min<sup>-1</sup> using BDD electrode. B) Comparison on the degradation of DEP with BDD, DSA and PbO<sub>2</sub> anodes, conditions in figure 1 A). C) HPLC chromatograms as function of time in DEP degradation, conditions as figure 1 A).

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### Peroxo-aided Photo-electrolysis of Rhodamine B

Danyelle Medeiros de Araújo<sup>1</sup>, Cristina Sáez<sup>2</sup>, Pablo Cañizares<sup>2</sup>, Carlos Alberto Martínez-Huitle<sup>1,\*</sup>,

Manuel Andrés Rodrigo Rodrigo<sup>2</sup>

<sup>1</sup> Federal University of Rio Grande do Norte, Instituto de Química, Lagoa Nova CEP 59078-970 - Natal, RN, Brazil

<sup>2</sup>Department of Chemical Engineering. Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain.

130/1 Ciudaa Keai, Spain.

danyelle.quimica@yahoo.com.br

Electrochemical oxidation of organics has been a key topic in environmental electrochemistry for the last two decades with two main research lines: development and testing of new electrode materials and combination of electrolysis with other technologies [1-2]. Nowadays, combination of anodic oxidation with other processes such as oxidants production, ultraviolet light (UV) irradiation or ultrasound (US) irradiation is becoming the new technological challenge [3-4] with highly efficient technologies as relevant as the electro-Fenton or the photo-electrolysis which are enlarging the range of applicability of electrolysis in the lower limit of concentration from the 1500 mg dm<sup>-3</sup> of the single electrolysis to very much lower concentrations of pollutants [5-7] and hence, they are expanding the range of applicability from the treatment of industrial wastes to other very interesting problems, such as reclaiming of urban wastewater and removal of persistent pollutants in diluted flows [8]. This work aims at giving light about the mechanisms of the electrolysis of organic pollutants during the treatment of wastewater containing sulfate and phosphate salts as supporting electrolytes. To do this, the treatment of synthetic wastewater containing Rhodamine B is assessed by electrolysis, photoelectrolysis and chemical oxidation with the oxidants produced electrolytically from a sulfate or phosphate solution. Results show that Rhodamine B was effectively oxidized by electrolysis and by chemical oxidation with the oxidants produced during the electrolysis of sulfate or phosphate solutions (peroxodisulfate and peroxodiphosphate, respectively). Light irradiation has a very positive effect during the electrolysis of RhB being this effect is greater at high current densities. However, this effect was much lower in the case of the chemical oxidation with peroxosulfates and peroxophosphates produced electrolytically. This behavior is explained in terms of the effect of the direct electrochemical oxidation processes and by the activation of oxidants in the bulk of the electrolytic treatment by production of highly efficient radicals.

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## Electrochemical Detection of Bisphenol A at a Carbon Nanotubes-NiO Nanoparticles Electrode

Lorena Athie Goulart, Lucia Helena Mascaro Department of Chemistry, Federal University of São Carlos – SP- Brazil lorenaathie@hotmail.com

Bisphenol A [2,2-bis (4-hydroxyphenyl) propane, BPA] is an organic compound that widely used in the plastic industry as a monomer for producing epoxy resins and polycarbonate [1]. A large number of researches have shown that BPA is an estrogenic contaminant, which may lead to breast cancer, prostate cancer, birth defect, infertility, diabetes and obesity [2]. Therefore, it is very important to remove BPA from the environment and to determine its presence in low concentrations. Various sensors have been used for the determination of BPA, being the most commonly used electrodes modified with carbon nanotubes (CNTs). In the other side, nickel nanoparticles (NiONPs) have been extensively used in electrode modification on account of its extraordinary catalytic activities and high conductivities. This work reports the electrochemical determination of BPA using glassy carbon electrode (GC) modified with carbon nanotubes (CNTs) and (NiONPs). CNTs multiple wall (MWCNT) were functionalized with sulfonitric solutions (3H<sub>2</sub>SO<sub>4</sub>:1HNO<sub>3</sub>), and dispersed in dimethylformamide for the manufacture of electrodes GC/CNTs. The GC/CNTs electrode was modified with NiONPs using cyclic potential (40 scans between 0 and -0.8 V at a scan rate of 100 mV s<sup>-1</sup>) in pH 4 maintained by an acetate buffer solution containing 2 mM of nickel nitrate [3]. Then, the potential was repetitively cycled (40 scans) from 0 to 0.6 V at scan rate of 100 mV s<sup>-1</sup> in fresh NaOH solution (0.1 mol  $L^{-1}$ ) for electrodissolution and passivation of nickel oxide layer at GC/NTCs. The concentration of nickel solution and the number of cycles in the electrodeposition were studied. Morphological characterization of GC/NTCs/NiONPs electrode was carried out by SEM and the presence of NiONPs was observed. The electrochemical behavior was evaluated by cyclic voltammetry and electrochemical impedance spectroscopy using solutions of BPA and  $K_4$ [Fe(CN)<sub>6</sub>] and the results were compared with those of GC. The modified GC/NTCs/NiONPs electrode shows the lower charge transfer resistance. The electrochemical detection was developed using square wave voltammetry (SWV) or differential pulse voltammetry (DPV). The cyclic voltammetry results showed an increase in the analytical signal and under the optimal conditions, the oxidation current in the analytical curves, increased linearly with increasing the concentration of BPA and the detection limit of 7.6 x 10<sup>-8</sup> mol L<sup>-1</sup>.

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## Electrochemical Surface Rehydrogenation of Boron-Doped Diamond Electrodes After an Electrochemical Polishing Process

<u>Ricardo F. Brocenschi</u>, Kallyni Irikura, Naihara Wächter, Romeu C. Rocha-Filho Dep. of Chemistry, Universidade Federal de São Carlos, São Carlos – SP, Brazil \*ricardo.fbro@gmail.com

Diamond is an electrical insulator that conducts heat even more efficiently than copper and can withstand very high electric fields [1]. High-quality diamond thin films, whose electronic properties are controlled by doping, can be reproducibly produced by chemical vapor deposition (CVD). Doping of CVD polycrystalline diamond with either *p*-type (such as boron) or *n*-type (such as phosphorus and nitrogen) dopants is possible [2]. Several factors are known to strongly affect the electrochemical properties of CVD polycrystalline diamond films: (i) non-diamond carbon impurity phases, (ii) surface termination (H vs. O), (iii) dopant type, level, and distribution, (iv) grain boundaries and other morphological defects, and (v) primary crystallographic orientation [3]. High-quality boron-doped diamond (BDD) thin films are being widely investigated [4–7]. As noted by Xu et al. [8], there are distinct characteristics that good BDD electrodes should exhibit: a low and stable background current in both the voltammetric and amperometric detection modes; a wide working potential window in aqueous media due to the high overpotentials for oxygen and hydrogen evolution, weak molecular adsorption, and relatively rapid electron-transfer kinetics for many aqueous redox systems without conventional pretreatment. However, as noted by Panizza et al. [9], the structure of diamond thin films grown by CVD may contain nonuniform grain sizes, randomly oriented crystals, non-diamond impurities, as well as surface roughness that limit their usefulness in many applications. Electrochemical polishing (EP) of BDD electrodes in the presence of an organic acid leads to surface smoothing, a reduced background current and lower doublelayer capacitance [9]. On the other hand, electrochemical polishing can introduce oxygen species on the BDD surface, which can be irreversible and damage the electrochemical active area [10]. In this context, the effects of an electrochemical polishing (EP) of BDD electrodes and a rehydrogenation of their surface by a cathodic pretreatment (CPT) were investigated. EP was carried out for different times (t = 5, 10, 20, 40, and 60 min) using an aqueous 3 mol L<sup>-1</sup> CH<sub>3</sub>COOH + 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and j = 1 A cm<sup>-2</sup>. Afterwards, CPT was performed: j = -160 mA cm<sup>-2</sup> for 480 s. The BDD electrode had an exposed geometric area of 0.32 cm<sup>2</sup>, the counter electrode was a Pt foil (1.0 cm  $\times$  0.5 cm), and a homemade saturated hydrogen electrode (0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub>) was used as reference. In potential window studies by cyclic voltammetry, oxidation peaks at  $\sim 2.4$  and  $\sim 1.4$  V were detected before and after both EP and CPT. This peaks are attributed to C=O and CH<sub>2</sub> species, respectively, which would likely be present at diamond grain boundaries [10]. The C<sub>dl</sub> values obtained after different EP times, for the EP-BDD and EP-CPT-BDD electrodes, increased three times; from values close to 5  $\mu$ F cm<sup>-2</sup> ( $t_{\rm EP} = 5$  min) to 15  $\mu$ F cm<sup>-2</sup> ( $t_{\rm EP} = 60$  min). These results indicate that  $C_{\rm dl}$  values increase with EP time due to the incorporation of oxygen species on the BDD surface, since these values do not change significantly when CPT is applied. However, although  $C_{dl}$  values did not change significantly after CPT, the electrochemically active area increases from ~0.54 to ~0.74 cm<sup>2</sup> and electron transfer kinetics increases considerably, since the  $\Delta E_{\rm p}$ value ( $v = 100 \text{ mV s}^{-1}$ ) for the redox pair [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> (0.1 mmol L<sup>-1</sup> in 0.1 mol L<sup>-1</sup> KCl) decreases e.g. from ~160 mV to ~100 mV, for EP = 10 min and PTC, respectively. Since no significant changes of the electrochemical response occur for EP times greater than 10 min, this procedure can be a useful tool to reduce the amount of non-diamond impurities on the BDD surface, followed by the reintroduction of hydrogen species by CPT, thus increasing the electrochemically active area and electron transfer kinetics.

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## Application of Boron Doped Diamond Electrode in Removal of Azo Dye Reactive Black 5

<u>Vanessa M. Vasconcelos</u><sup>a</sup>\*, Fernanda L. Migliorini<sup>b</sup>, Juliana R. Steter<sup>a</sup>, Maurício R. Baldan<sup>b</sup>, Neidenêi G. Ferreira<sup>b</sup>, Marcos R. V. Lanza<sup>a</sup>

<sup>a</sup>University of Sao Paulo - Institute of Chemistry of Sao Carlos – 13566-590 - Sao Carlos – SP- Brazil <sup>b</sup>Instituto Nacional de Pesquisas Espaciais, 12245-970, São José dos Campos, SP, Brazil \*vanessavasconcelos@iqsc.usp.br

Reactive Black 5 (RB-5) dye is an azo dye since it contains R-N=N-R' as chromophoric group. RB-5 dye presents low efficiency of fixation on the fiber due to the competition between the reaction of the vinvlsulphone group to fix on the fibers and the reaction of hydrolysis of the vinvlsulphone group that produced the 2-hydroxyethylsulfone, which does not fix on the fiber. Therefore, it can be easily lost to wastewater. In addition RB-5 was considered a moderately toxic by Ramsay[1] with  $50\% > EC_{20} > 25\%$ and Gottlieb [2] determined the EC5030min to the hydrolyzed and non-hydrolyzed form to RB-5 dye as  $11.49 \pm 3.68 \text{ mgL}^{-1}$  and  $27.59 \pm 4.01 \text{ mgL}^{-1}$ , respectively, against *Vibrio fischeri* bioluminescent bacteria; the author still considered the hydrolyzed form of RB-5 as weak genotoxic. Due to this is important to treat this dye before to dispose it into the environment. In this context, the main of this present work was to study the degradation of Reactive Black 5 dye using a no commercial Boron Doped Diamond (BDD). A one-compartment cell was used with a Pt wire electrode as counter electrode and a commercial reference electrode (Ag/AgCl in 3 mol L<sup>-1</sup> KCl). BDD was doped with 15,000 ppm B/C and has a geometric area of 4.15 cm<sup>2</sup>. Electrolysis were carried out by applying different current density (10, 25, 50, 75 and 100 mA cm<sup>-2</sup>). The electrolyte (0.40 L) was an aqueous solution containing 50 mg  $L^{-1}$  of RB-5 dye. To monitor the efficient of the degradation, samples was taken in different times of electrolysis and analysed using UV-Visible (UV/VIS) Spectrophotometry (200-800 nm), High Performance Liquid Chromatographic (HPLC) and TOC-VCPN analyser. Also, the degradation intermediate compounds was identified using a mass spectrometer LTQ-Orbitrap Veloz high resolution analyser. BDD film supported in titanium without delaminations or cracks was grown by hot filament chemical vapour deposition technique and the quality of BDD film was measured using scanning electron microscope images and Raman. Degradation results showed that BDD films was able to remove RB-5 dye and to promote total colour and TOC removal. The decolorization of RB-5 followed the zero pseudo order reaction kinetics and increased in current density improved the kinetics of degradation reaction. In addition 90% of chromatographic area ( $\lambda$ =311 nm) was removed that meaning the cleavage of the aromatic ring. Total colour removal was achieved within 40 min of electrolysis applying 100 mA cm<sup>-2</sup> while total mineralization was noted within 8 h of electrolysis. This finding proved that promoted total mineralization is harder than removed total colour because other organic compounds as naphtol, quinones, anthraquinones, hydroquinone, benzoic acid, catechol, phthalic, anhydride among others were formed during the electrolysis until formed phenol and aliphatic acids as oxalic acid, which can be easily converted to CO<sub>2</sub>. Therefore, BDD/Ti electrode can be an alternative material to be applied in degradation of RB-5 dye.

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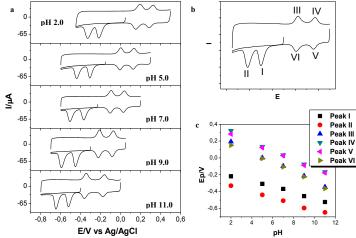
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# Multiwalled carbon nanotubes-glassy carbon electrodes for electrochemical study of 2,7-dinitro-9-fluorenone adsorbed.

Julio Urzúa, Claudia Yañez, José Marco, Juan Arturo Squella Faculty of Chemical and Farmaceutical Sciences. Universidad de Chile Sergio Livingstone Pohlhammer 1007. Independencia. Santiago. Chile. P.O. Box 8380492. j.urzua@ciq.uchile.cl

The electrochemistry of nitroaromatics deposited on glassy carbon electrodes (GCE) is well known [1, 2], but voltammetric peaks of the characteristic signals with a good resolution are not obtained. Using a multiwalled carbon nanotubes-glassy carbon electrode (MWCNT-GCE) increases the electroactive area and the number of sites for adsorption in both the electrode surface and into the nanotubes net. Also taking advantage of the high electrical conductivity of MWCNT and their chemical inertness, it can be obtained more intense and well-resolved voltammetric peaks, without possible side-reaction signals between the adsorbed species and the nanomaterial in the electrode surface. By reducing the nitro group in nitroaromatics it can be possible to obtain a derivative hydroxylamine/nitroso redox couple, which is more stable in a MWCNT-GCE [3] than in a bare GCE [1] respect to the time and the number of scans.



In this research we study the electrochemical behavior of 2,7dinitro-9-fluorenone (2,7-NFN) when it is adsorbed onto a MWCNT-GCE. A study of pH effect on 2,7-NFN can't be done due to its low solubility in aqueous media, but when the nitroaromatic is adsorbed onto a MWCNT-GCE, we observed a pН influence upon the voltammetric peaks of 2-7-NFN in the electrode surface.

The Ep vs pH graphs show no breaks in the corresponding slopes, which means that there's no mechanism changes in a pH range of 2-11 (Figure 1).

**Figure 1**. **a)** pH effect on 2,7-NFN- MWCNT-GCE, in Britton-Robinson 0,1 M buffer. **b)** assignment of signals. **c)** Ep vs pH graph for a 2,7-NFN- MWCNT-GCE.

2,7-NFN is a nitroaromatic compound containing in its structure two nitro groups which can be reduced to hydroxylamine. When only one nitro group is reduced and the other nitro group remains without reducing, we observed that the stability of the generated redox couple is greater than when two nitro groups are reduced and two redox couples are generated.

XPS studies of this modified surfaces show the characteristic binding energy of the nitro and hydroxylamine groups, demonstrating a correct modification and derivatization processes respectively. However it was not possible to differentiate the presence of the nitro and nitroso groups, because of its similar binding energies.

#### Acknowledgments

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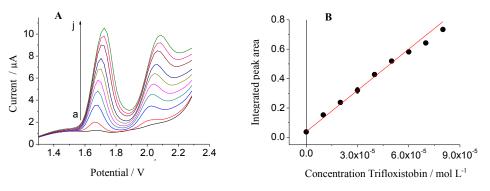
## Voltammetric determination of trifloxystrobin in orange juice and water samples using the boron-doped diamond electrode

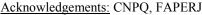
Joseany de M. S. Almeida<sup>a\*</sup>(PG); Rafael M. Dornellas<sup>a</sup>(PQ); Ricardo Q. Aucélio (PQ)<sup>a</sup>

<sup>a</sup> Department of Chemistry, Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro. \*joseanyqm@hotmail.com

The doping of diamond with boron generates attractive electrochemical sensing characteristics and useful in voltammetry and amperometry<sup>1</sup>. Boron-doped diamond electrode (BDDE) allows a wide potential window in aqueous solutions, shifting the electrolysis of water and dissolved oxygen to values beyond  $\pm$ 2200 mV. This enables the determination of chemical species that cannot be detected using electrodes based on glassy carbon as substrate. Because of the BDDE, it was possible to quantify trifloxystrobin at +1734 mV. Trifloxystrobin is a pesticide used to combat fungi in several types of crops. Despite its low toxicity and rapid degradation, studies must be performed to assess levels human exposure to such a substance<sup>2</sup>. Square-wave anodic voltammetry was used and the determination was performed in Britton-Robinson buffer (0.04 mol  $L^{-1}$ ; pH 4.00)/acetonitrile 70/30% v/v. The sample volume added in the cell was 1.00 mL and the quantification made using the analyte addition procedure. The activation of the working electrode was made using galvanostatic chronopotentiometry and cyclic voltammetry. The typical analytical addition curve is shown in Figure 1 with the analytical response  $Y = (8.8 \times 10^{-3} \pm 4.9 \times 10^{-3} \pm 4.9$  $10^{-5}$ ) X + (3.8 x  $10^{-8} \pm 1.5$  x  $10^{-9}$ ) and linear behavior indicated by  $R^2 = 0.998$ . The following experimental conditions were used: amplitude = 0.04 V; frequency = 30 Hz; step potential = 0.02 V. The instrumental limit of quantification was 2.4 x  $10^{-6}$  mol L<sup>-1</sup> and accuracy was about 7% at the concentration level of 4 x 10<sup>-6</sup> mol L<sup>-1</sup>. The samples analyzed were fortified with the analyte (see fortification values and recoveries in parenthesis): i) water from the Rainha creek (4.5 x  $10^{-6}$  mol L<sup>-1</sup> and 89.3 %), ii) water from Lagoa Rodrigo de Freitas ( $4.5 \times 10^{-6} \text{ mol } \text{L}^{-1}$  and 91.2 %), iii) tap water ( $4.9 \times 10^{-6}$ mol L<sup>-1</sup> and 98.0 %), iv) mineral water (4.6 x  $10^{-6}$  mol L<sup>-1</sup> and 92.8 %) and v) orange juice (4.1 x  $10^{-6}$  mol  $L^{-1}$  and 82.0 %). A study to evaluate potential interferences was made in the presence of other similar fungicides (strobiluins). Kresoxim-methyl, picoxystrobin and fluoxastrobin were found to interfere with the method when the trifloxyxtrobin/strobilurin) molar ratios were respectively 1:2; 1:2 and 1:1 due to the proximity of the oxidation peaks form these strobilurins with the ones of the analyte. Diagnostic studies indicated that oxidation of trifloxystrobin in aqueous medium at the surface of the boron-doped diamond is irreversible and involves two electrons and it is probably from the oxidation of the aromatic and alkyl aromatic hydrocarbons in the analyte structure.<sup>3</sup> The UV degradation of trifloxystrobin was evaluated using the proposed electrochemical method and a the kinetics of degradation established.

**Figure 1.** A- Standard addition of trifloxystrobin (sequence of voltammograms and analytical curve measured at  $E_{p1} = +1734 \text{ mV}$ ) in creek water sample using square-wave anodic voltammetry with DDBE (concentration of analyte varying from a) 1 x 10<sup>-5</sup> to j) 8 x 10<sup>-5</sup> mol L<sup>-1</sup>). B- Analytical curve.





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# Electrochemical treatment with BDD anode of soil-washing effluent polluted with atrazine: Influence of particle size

Santos, E.V<sup>1</sup>, C. Sáez<sup>2</sup>, Martínez-Huítle, C. A.<sup>1</sup>, Cañizares, P.<sup>2</sup>, M.A. Rodrigo<sup>2</sup> <sup>1</sup>Federal University of Rio Grande do Norte, Natal, Brazil <sup>2</sup>Universidad de Castilla-La Mancha, Ciudad Real, Spain e-mail: elisama quimica@yahoo.com.br

The significance of size distribution of pollutants is long recognized for the interpretation of wastewater characteristics, assessment of appropriate treatment technologies and estimation of expected removal performances. In this context, the objective of this study was to evaluate the role of particle size distribution during the electrolysis with BDD anodes, sono-electrolysis (US) and photo-electrolysis (UV-electro) of surfactant-aided soil washing effluents polluted with atrazine. The surfactant-aided soil-remediation was carried out in a stirred batch tank. To do this, low-permeability soil (1000 g) polluted with 100 mg of atrazine (used as model pollutant) and 800 cm<sup>3</sup> of solubilizing agent (deionized water solutions containing 100-5000 mg dm<sup>-3</sup> of surfactant and 500 mg dm<sup>-3</sup> of NaHCO<sub>3</sub>) were used. Total organic carbon (TOC), chemical oxygen demand (COD), size particles and z-potential were monitored during galvanostatic electrolysis of soil-washing effluent (700 dm<sup>-3</sup>) using BDD anodes by applying 30 mA cm<sup>-2</sup> at 25 °C.

Results showed that TOC and COD parameters decreased with the electrical charge passed. However, the TOC and COD decay seem to be very similar up to pass 14 Ah dm<sup>-3</sup>, after that, the rate of TOC removal increased until its complete elimination. Conversely, COD elimination was completely attained when 43 Ah dm<sup>-3</sup> was attained. The emulsion generated by the presence of surfactant and atrazine is broken during electrolysis, favoring the elimination of organic matter trapped by surfactant, confirming the fast TOC decay. However, the fragmentation of surfactant limit the complete elimination of organic content, but the dissolution of sulfate ion in aqueous media promotes the electrogeneration of peroxodisulphates (2SO<sub>4</sub><sup>2-</sup>  $\rightarrow$ S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + 2e<sup>-</sup>) on BDD surface. It contributes to complete the degradation of remaining atrazine as well as part of the organic surfactant. The existence of two behaviors during the electrolysis, before and after 13 Ah dm<sup>-3</sup>, is related to the particle size. In fact, the particle size decreases rapidly during the first stages of the electrochemical process, especially when dispersed particles are present in the solution. When the particle size achieved a small size, its elimination was faster. Regarding sono-electrolysis and photoelectrolysis treatments, synergistic effects of irradiating UV light and sonication are clearly observed in both oxidation rate and break-up emulsion, due to the improvement of mass transfer to the conductivediamond surface in the case of US irradiation, and to the massive formation of radicals in the bulk solution from oxidants produced electrochemically in the case of UV light irradiation.

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## Electrocatalytic Oxidation of Organic Contaminants Using TiO<sub>2</sub>/BDD/Ti Composite Electrode

A.B. Couto\*, F.L. Migliorini, M.R. Baldan, N.G. Ferreira Instituto Nacional de Pesquisas Espaciais – INPE Av. Dos Astronautas, 1758, São José dos Campos, Brazil abcouto@yahoo.com.br

The population growth as well as the industrial negative impact on natural water sources led to significant increases in the volumes of wastewater, which has raised widespread concern for its toxicity. As a result, several technologies have been developed for more effective wastewater treatment. Currently, electrochemical catalysis technologies are widely used as advanced oxidation processes for wastewater treatment, especially for the environmental remediation by abatement of organic and inorganic pollutants due to its high efficiency, versatility, safety and environmentally friendly [1]. The role of the catalyst in the catalytic processes consists in increasing the rate and controlling the selectivity of the chemical reactions involved. Owing to the high chemical stability of its surface, even being anodically polarized in acidic medium, associated with a wide potential window for water discharge and low background current, makes boron doped diamond (BDD) an interesting electrode substrate for the catalyst deposition [2] in heterogeneous catalysis.  $TiO_2$  is the most useful oxide material for application in electrocatalysis due to its stability in alkaline and acidic media, non-toxicity and low cost. Moreover, provides rather high electrochemically active surface areas, making it a suitable catalyst. Thus, the TiO<sub>2</sub>/BDD composite systems appear as a very interesting electrode for advanced oxidative process. In this sense, the aim of this work was to study the influence of the doping level on BDD in the anodic hydrolysis of TiCl<sub>3</sub> for obtaining TiO<sub>2</sub>/BDD composites. These composites will be discussed considering their performance in the Brilliant Green dye electrooxidation process in terms of the composite characteristics associated to the electrode doping level. BDD films were grown by hot filament-assisted chemical vapor deposition technique on the titanium substrate, activated by methane hydrogen gas mixture with a pressure of 40 Torr and temperature around 650°C for 24 h. Boron source was obtained by an additional hydrogen line passing through a bubbler containing  $B_2O_3$  dissolved in methanol with a controlled B/C ratio that led to films with different doping level. The TiO<sub>2</sub> electrodeposition on BDD films was performed under potentiostatic mode, at a fixed potential of 0.6 V during 3 min in a 50 mmol L<sup>-1</sup> TiCl<sub>3</sub> (pH=2) aqueous solution. Electrochemical measurements were made using a platinum mesh as a counter electrode and Ag/AgCl/KCl<sub>(sat)</sub> as the reference electrode. The electrooxidation experiments were performed at current density of 100 mA cm<sup>-2</sup> using 100 mg L<sup>-1</sup> of the Brilliant Green dye and K<sub>2</sub>SO<sub>4</sub> 0,1 mol L<sup>-1</sup>, in a total treatment time of 300 min. The Brilliant Green dye electrochemical degradation was monitored by UV-Visible (UV/VIS) Spectrophotometry and Total Carbon Organic. High deposit uniformity of TiO<sub>2</sub> was observed at the grain faces by scanning electron microscopy for highly doped BDD compared to that for the lightly doped BDD. The X-ray diffraction measurements showed rutile TiO<sub>2</sub> crystallographic forms for both depositions. Concerning Brilliant Green dye eletrooxidation, the results showed that both TiO<sub>2</sub>/BDD electrodes were efficient in the degradation. The lightly doped electrode, presents highest diamond purity, as a consequence, the TiO<sub>2</sub> deposits did not enhance significantly the dye degradation. On the other hand, the  $TiO_2$  influence was more pronounced on highly doped diamond electrode, probably due to this electrode present the strong influence of  $sp^2$  content.

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## Electrooxidation of the Textile Dye Using Boron Doped Diamond Electrodes with Different Doping Levels and sp<sup>2</sup> Content

F.L.Migliorini<sup>a</sup>, M.R.V. Lanza<sup>b</sup>, M.R. Baldan<sup>a</sup> and N.G. Ferreira<sup>a</sup> <sup>a</sup>Instituto Nacional de Pesquisas Espaciais, INPE. Avenida dos Astronautas, 1758, Jardim da Granja, cep: 12227-010, São José dos Campos- SP. <sup>b</sup>Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, Brasil. fernandamigliorini@yahoo.com.br

Industrial pollutants are known due to their toxicity and persistence in the environment. Several methods have been studied to eliminate or to decrease the toxic effects of these compounds [1]. Among these methods, EAOP (electrochemical advanced oxidative processes) have been used with success and they are based on the in situ electrogeneration of highly reactive hydroxyl radical (•OH). Thus, it is a promising environmental technique [2]. The most problem is the chosen of anode material which should be stable, resistant and efficient. BDD (boron doped diamond) anodes are used with success on the organic compound treatment and the mechanism involves hydroxyl radical generation physically adsorbed. BDD film can be grown on several substrates but titanium (Ti) substrate has shown mechanical resistance to industrial application [3-5]. Thus, this work presents the production and characterization of BDD/Ti films deposited with different  $sp^2$  contents and levels doping applied to Brilliant Green dye electroxidation. Films were grown on substrate of 2.5 x 2.5 cm by hot filament chemical vapor deposition technique at  $CH_4$  additions of 1, 2, 6 and 10 sccm diluted in  $H_2$  for a total flow rate of 200 sccm. The boron source was obtained from a constant flow of 40 sccm for an additional H<sub>2</sub> line passing through a bubbler containing the B<sub>2</sub>O<sub>3</sub> dissolved in methanol with B/C ratio of the 2000, 7000, 15000 and 30000 ppm. Top view SEM images of BDD films were obtained from a Jeol equipment JSM 5310. The quality of BDD films were analyzed from Micro-Raman spectra recorded by a Renishaw microscope system 2000 in backscattering configuration and by X-ray Diffraction. Electrochemical measurements were made using a platinum mesh as a counter electrode and Ag/AgCl/KCl<sub>(sat)</sub> as the reference electrode. The electrooxidation experiments were performed at current density 100 mA cm<sup>-2</sup>, using 100 mg L<sup>-1</sup> of the Brilliant Green dye and  $K_2SO_4$ 0,1 mol L<sup>-1</sup>, in a total treatment time of 300 min. The Brilliant Green dye electrochemical degradation were monitored by: (1) UV Visible (UV/VIS) Spectrophotometry, and (2) Total Carbon Organic. The top view SEM images show continuous and homogeneous films covering the entire substrates. Visible Raman spectroscopy confirmed the good quality of the BDD films by the presence of the narrow band at 1332 cm<sup>-1</sup> corresponding to diamond signature The effect of boron doping was also observed in the spectrum features. The diamond peak decreased in intensity with the B increase in BDD films. Two bands appeared associated to sample doping. The band at 1200 cm<sup>-1</sup> increased significantly by increasing the doping level associated to the disorder promoted by B inclusion in diamond lattice while the band at 500 cm<sup>-1</sup> is concerning the B pair vibrations. X-ray diffraction showed diamond diffraction planes, assuring the material crystallinity. Besides, it was identified carbides (TiC) and hydrides (TiH) patterns in the film/substrate interface. The results showed that all BDD/Ti electrodes were efficient in the degradation of Brilliant Green dye. Particularly, the measurements showed the best dye degradation efficiency for electrode grown with 15000 ppm and with the lowest CH<sub>4</sub> concentration. It presented the best solution decolourisation efficiency in addition to its greatest efficiency in the organic compound mineralization. This behavior was associated with its highest diamond purity taking into account the  $CH_4$ addition as well as the suitable doping level.

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## Exploring the Electroanalytical Performance of Porous Diamond-Like Carbon Electrodes Grown on Vertically Aligned Carbon Nanotubes

<u>Orlando Fatibello-Filho</u><sup>a,\*</sup>, Tiago A. Silva<sup>a</sup>, Hudson Zanin<sup>b</sup>, Paul. W. May<sup>c</sup>, Evaldo J. Corat<sup>b</sup> <sup>a</sup>Department of Chemistry, São Carlos Federal University, São Carlos-SP, Brazil <sup>b</sup>National Institute for Space Research, São José dos Campos-SP, Brazil <sup>c</sup>School of Chemistry, University of Bristol, Cancocks Close, Bristol BS8 1TS, United Kingdom

\*bello@ufscar.br

Diamond-like carbon (DLC) is an interesting metastable form of amorphous carbon that contains a mixture of tetrahedral  $(sp^3)$  and trigonal  $(sp^2)$  carbon hybridisations in varying amounts depending on its deposition conditions [1]. DLC films shows chemical inertness, optical transparency, high mechanical hardness and very high electrical resistance [2]. Thus, unmodified DLC films are electrically insulating, which has forbidden their application in several fields, including electroanalytical. To overcome this problem, in this work DLC films were deposited on a vertically aligned carbon nanotubes (VACNT) array, providing a highly porous and conductive composite material formed totally by carbon [3]. Firstly, VACNT were prepared on Ti substrates by microwave plasma chemical vapour deposition [4] and, in a second experiment, thin DLC layers cover were produced by plasma-enhanced chemical vapour deposition [3]. The electroanalytical performance of the DLC:VACNT electrode was explored to determination of target molecules such as dopamine (DA), epinephrine (EP) (neurotransmitters) and acetaminophen (AC) (an endocrine disruptor). From cyclic voltammetry experiments conducted at different scan rates, the electron transfer kinetic of these molecules on the DLC:VACNT surface was investigated, and high values of heterogeneous electron-transfer rate constants  $(k^0)$  were obtained:  $k^0$  (DA) =  $5.2 \times 10^{-3}$  cm s<sup>-1</sup>,  $k^0$  (EP) =  $8.9 \times 10^{-3}$  cm s<sup>-1</sup> and  $k^0$  (AC) =  $4.5 \times 10^{-3}$  cm s<sup>-1</sup>. Using simple and lowcost techniques such as cyclic voltammetry, analytical curves in the concentration range from 10 to 100  $\mu$ mol l<sup>-1</sup> were obtained and excellent analytical parameters achieved, including high analytical sensitivity and low limits of detection of 2.9, 4.5 and 2.3 µmol l<sup>-1</sup> for DA, EP, and AC, respectively. The results demonstrate the electroanalytical potential of the novel DLC:VACNT electrode for the determination of important target analytes, and other investigations into the use of these DLC:VACNT electrodes as electrochemical sensors and DPV and SWV techniques to detect organic and inorganic compounds in different sample matrices are underway in our groups.

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### Diamond anodes for the production of high value oxidants

J.F. Pérez-Serrano, M.J. Martín de Vidales, S. Cotillas, J. Llanos, C. Sáez, <u>M.A. Rodrigo</u>, P. Cañizares Department of Chemical Engineering. Faculty of Chemical Sciences and Technologies. University of Castilla La Mancha. Campus Universitario s/n 13071 Ciudad Real. SPAIN Manuel.Rodrigo@uclm.es

Production of hydroxyl radicals during water discharge, ready to interact with the electrolyte is the main characteristic of the application of diamond anodes in the electrolysis of aqueous solutions. It explains the high efficiencies obtained in the treatment of wastewater and it also helps to understand its appropriateness to be applied in the production of oxidants with high efficiencies. This lecture aims to summarize the state of the art of the technology based on the experience of the authors with this advanced carbon material. To do this, results obtained in our lab on the production of different types of oxidants such as peroxocompounds (peroxosulphate, peroxophosphate, peroxocarbonate and peroxoacetate), perhalogenated anions (perchlorate and perbromate) and ferrates are analyzed, pointing out the advantages and drawbacks of the technology. Special attention is paid to the storage and activation of the lab. The lecture also faces the challenges of the technology for the near future (electrode manufacturing, reactor engineering, coupling with irradiation technologies, scale-up, cost optimization...) pointing out the direction in which research and engineering studies have to be carried out in order to attain attractive processes which could be implemented at the industrial scale.

#### Acknowledgements

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## Development of Ti/TiO<sub>2</sub>/CNTs Films to Use as Cathode for Hydrogen Evolution Reaction

Lucia H. Mascaro, Fernando C. Moraes, F. Willian de S. Lucas Chemistry Department, Federal São Carlos University Rod. Washington Luiz, km 235- São Carlos- SP- Brazil Imascaro@ufscar.br

Water electrolysis is an ideal method to produce highly purified hydrogen for large-scale. However, lowering the electrolytic energy consumption is needed in order to make the method economically. One of the most effective ways to minimize the energy consumption is to reduce the hydrogen evolution overpotential in the electrolysis process. Therefore, the development of highly active and stable electrode materials as hydrogen cathodes is significant in the hydrogen energy system and electrolysis industry. TiO<sub>2</sub> is considered as one of the most useful photocatalysts due its broad functionality, long-term stability and non-toxicity. Pure and modified  $TiO_2$  in different morphologies have been employed as photoanode at water splitting. However, there are few papers describing the use of  $TiO_2$  as cathode for hydrogen generation. In this paper a composite of Ti/TiO<sub>2</sub>/CNTs (carbon nanotubes) was synthesized and used as cathode to hydrogen evolution reaction (HER). The Ti/TiO2/CNTs films were synthetized by sol-gel and dip-coating method using compositions similar to the ones described by Sánchez and Rincón. The sol-gel was obtained by mixing 100 mg of multiwall carbon nanotubes previously functionalized. A cleaned, polished and smoothed titanium plate was dipped into the sol-gel and placed in an oven at 400°C for 5 min, after each dipping-withdrawing process. The dip-coated films were subjected to 25 dippingwithdrawing-annealing cycles, before being sintered at 400°C for 60 min. The films were characterized by FEG-SEM, XRD and UV-vis spectrometer. The electrocalytic activity for HER of Ti/TiO<sub>2</sub>/CNTs films was evaluated in 1.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution by linear voltammetry at 0.1 mV s<sup>-1</sup>. The electrochemical measurements were performed in a conventional three-electrode cell using a potentiostat/galvanostat AUTOLAB coupled with a microcomputer. All potentials are referred to the saturated calomel electrode (SCE) and the auxiliary electrode was a large surface of platinum spiral wire. In long-term electrolysis experiments, the coating electrodes were tested with a constant potential of -0.4 V at 25° C.

SEM images shows that films consist of TiO<sub>2</sub> aggregates with CNTs homogenously distributed (Figure 1a) and XRD analysis shows that the films contain anatase TiO<sub>2</sub> phase. The Figure 1b present the curves obtained in 1.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> for Ti/TiO<sub>2</sub>/NTCs, Ti/TiO<sub>2</sub> and Pt electrodes. The enhanced activities of Ti/TiO<sub>2</sub>/CNTs coatings, compared with the Pt and Ti/TiO<sub>2</sub> presented the smaller value for the hydrogen overpotentials. The results clearly demonstrate that the addition of CNTs at TiO<sub>2</sub> films results in an increased electrocatalytic activity in hydrogen evolution. The hydrogen evolution overpotential is 130 mV shifted for more negative potential compared at Pt electrode. Furthermore, the addition of CNTs to TiO<sub>2</sub> electrodes films led to a decrease of 250 mV of hydrogen evolution overpotential. This effect can not be attributed to an increase in surface roughness because the surface roughness, practically, no changes. The increased of the electrocatalytic activity in hydrogen evolution is an intrinsic activity of the material. Long-time electrolysis at a constant potential of -0.4 V showed the activity of Ti/TiO<sub>2</sub>/CNTs for hydrogen evolution was not changed, indicating the sufficient durability for practical electrolysis applications. Thus, the results showed that films Ti/TiO<sub>2</sub>/CNTs can also be used as cathodes in water splitting.

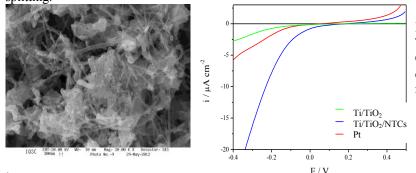


Figure 1: (a) SEM images of  $Ti/TiO_2/CNTs$  films and (b) Comparison of the HER for different electrodes at 1.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

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# Degradation of antihypertensive drugs losartan and hydrochlorothiazide in water by electro-oxidation with BDD. Application of method to tablets pharmaceuticals.

Ricardo Salazar, Nicole Contreras-Droguett

Laboratorio de electroquímica Medioambiental, LEQMA. Departamento de Química de los Materiales, Universidad de Santiago de Chile, USACh, Casilla 40, Correo 33, Santiago, Chile E-mail: <u>ricardo.salazar@usach.cl</u>

Due to the high number of patients with cardiovascular diseases, domestic production of antihypertensive drugs has increased considerably in the last 50 years. Daily are generate large volumes of wastewater industrial containing high concentrations of antihypertensive drugs. The low efficiency of conventional water treatments for the degradation of many emerging and bio-recalcitrant organic pollutants has promoted the research of alternative methods. In this way, electrochemical technology has received great attention for the prevention of pollution problems, as reported in several books and reviews.

In the present work was studied degradation and mineralization of antihypertensive drugs losartan and hydrochlorothiazide by electro-oxidation in water. 100 mL of solution containing 100 mg  $L^{-1}$  of Total organic carbon (TOC) of losartan and hydrochlorothiazide, were electrolyzed. 0.05 M Na<sub>2</sub>SO<sub>4</sub> was used as electrolyte support, in electrolytic cells are thermoregulated at 35 ° C for 3 hours. BDD electrode (boron doped diamond) was used as anode and a stainless steel cathode as anode, both with 5cm<sup>2</sup> geometric area exposed to the solution.

Experimental variables as initial pH and applied density current were evaluated.

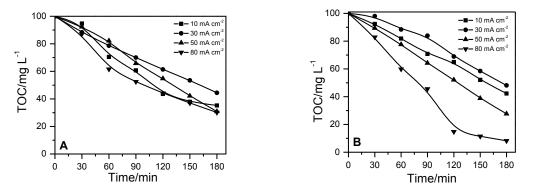


Figure 1. Effect of applied density current for the a batement of total organic carbon (TOC) of A) 0.377 mM losartan; and B) 1.188 mM of hydrochlorothiazide. Experimental conditions: 0.05 M of Na<sub>2</sub>SO<sub>4</sub>,  $T = 35 \degree C$ , pH 7.0.

In Figure 1 the total organic carbon abatement for both drugs is presented, applying different current densities. It is observed that most mineralization is achieved at high currents for both drugs after 3h of electrolysis.

Carboxylic acids and inorganic ions were determined during the oxidation process, besides degradation kinetics constant.

Commercial tablets each antihypertensive were also degraded by the process of oxidation.

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# Electrochemical determination of picoxystrobin on boron-doped diamond electrode: square-wave voltammetry vs. BIA-amperometry

Rafael M. Dornellas<sup>a</sup>\*, Rodrigo A. A. Muñoz<sup>a</sup>, Ricardo Q. Aucélio<sup>b</sup>

<sup>a</sup> Instituto de química, Universidade Federal de Uberlândia (UFU), Uberlândia-MG, Brazil. <sup>b</sup>Departamento de química, Pontificia Universidade Católica do Rio de Janeiro (PUC Rio), Rio de Janeiro, Brazil.

rafaeld or nell as @oi.com.br

The monitoring of pesticide residues is of capital importance for environment protection.<sup>1</sup> The strobilurin is a class of synthetic fungicides that inhibits the growth of fungus spores in its initial phase. Picoxystrobin belongs to the class of the strobilurins and has been used in plantations of fruit and vegetables. The acceptable daily intake of picoxystrobin is 43 µg kg<sup>-1</sup> in accordance with the Brazilian regulatory agency.<sup>2</sup> This work reports two new electroanalytical methods for picoxystrobin determination based on its electrochemical oxidation on a boron-doped diamond electrode (BDDE) after cathodic treatment. Square-wave voltammetry (SWV) of picoxystrobin was revealed two well-shaped peaks at 1.28 and 1.90 V. Cyclic voltammetry indicated that both oxidation processes are electrochemically irreversible, diffusion-controlled, pH independent, and the redox mechanism involves the transference of two electrons for each oxidation peak. The method based on SWV produced linear analytical response in the range between 0.7 and 20  $\mu$ mol L<sup>-1</sup> (R<sup>2</sup> > 0.994), relative standard deviation (RSD) of 5% (n=10) and the detection limit was 0.3  $\mu$ mol L<sup>-1</sup> (step of 5 mV, amplitude of 50 mV, and frequency of 30 Hz). The amperometric detection at the BDDE associated with batch-injection analysis (BIA) involved the injection of a plug of sample (or standard) directly onto the surface of the BDDE by placing the tip of the electronic micropipette at close a distance (2 mm) of the of the electrode. After quick injection, the analyte species in the plug diffuses to the large volume of electrolyte in which the three electrodes are immersed. The optimized BIA parameters were 13.3 mL min<sup>-1</sup> as dispensing rate and 50 µL as injection volume. The BIA method presented linear dynamic range between 5.3 and 100  $\mu$ mol L<sup>-1</sup> ( $\dot{R}^2 > 0.999$ ) and the detection limit was  $1.7 \,\mu$ mol L<sup>-1</sup>. Absence of memory effects were observed for continuous injections of standard solutions in two different concentration levels (5 and 10 µmol L<sup>-1</sup>). Although less sensitive, the BIA method present a higher analytical frequency of 108  $h^{-1}$  and more precise (RSD = 4%). The SWV method can be considered more selective than the amperometric method. In the amperometric detection, due to the high potential of detection (1.9 V), many possible interfering species can be oxidized. The presence of interfering species that oxidize at less positive potentials will not affect picoxystrobin determination by the SWV method if the peaks of analyte and interfering species are well resolved (about 100 mV separation). Both electroanalytical methods were applied for picoxystrobin determination in natural water samples spiked with known amounts of the pesticide. SWV determinations were performed using the analyte addition method and the BIA-amperometric determinations by interpolation in the analytical curve. Recovery values between 93-104% and 93-106% were obtained for the SWV and BIAamperometry, respectively. Therefore, both electroanalytical methods can be successfully applied for natural water analyses using a BDDE with different analytical characteristics.

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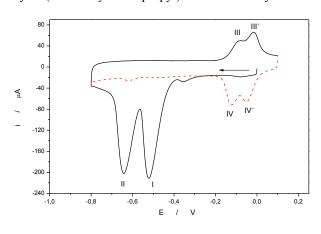
# Multiwalled carbon nanotube electrodes modified with encapsulated 3,5-dinitrobenzoic acid.

J.A.Squella<sup>1</sup>, J. Carbajo<sup>2</sup> and R. Moscoso<sup>1</sup>

<sup>1</sup>Dpto. Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas. Universidad de Chile. Chile. e-mail: asquella@ciq.uchile.cl. <sup>2</sup>Facultad de Ciencias Experimentales. Universidad de Huelva. Huelva, España.

The use of carbon nanotubes (CNTs) as working electrode has attracted the interest from the electrochemistry community in the last ten years. Their electronic characteristic and their specific properties such as surface-to-volume and porosity provide many interesting applications as electrode material. One of the most interesting applications is based in its feasibility to be modified according the requirement of the researcher. In the last years [1,2] we have designed CNTs electrodes modified by the encapsulation of the electroactive compound, i.e. nitrocompounds.

In a previous paper, Kubota et al., [3] revealed a modified electrode wherein 3,5-dinitrobenzoic acid was covalent attached to nanostructured platform. The procedure involved dropping an aliquot of  $5\mu$ L of a dispersion of CNT with polyethilenimine (PEI) and then dried under nitrogen atmosphere. After that, the electrode was dipped in 5 ml of ethanol containing 4.6 mg of N-hydroxysuccinimide (NHS), 4.8 mg of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and 10.0 mg of 3,5-DNBA for 1.5 h.



In this work we revealed a totally different way to modify the CNT electrode with 3,5-DNBA that does not involve a covalent attach but a encapsulation of the 3,5-DNBA in the 3-D network of the MWCNT on the glassy carbon electrode (GCE). The new procedure involved dropping an aliquot of  $5\mu$ L of a dispersion of 3 mg/mL of MWCNT with 1,3-dioxolane and then dried at room temperature [2]. After that, the electrode was dipped in a solution containing 3,5-DNBA in a pH 7 phosphate buffer for 4 minutes. After that the electrode was retired of the solution containing the nitro compound washed and immersed in a

solution containing only buffer and then the voltammogram of the enclosed figure was obtained. In the first cathodic scan we observed two peaks (I and II) each one corresponding to the reduction of the nitro group to the corresponding hydroxylamine derivative. In the back scan we observed two anodic peaks (III and III') each one corresponding to the oxidation of each hydroxylamine group to form the nitroso derivatives. In the second cathodic scan appeared two peaks (IV and IV') due to the back reduction of the nitroso derivatives to the corresponding hydroxylamine derivatives. Also, in the second cathodic scan no signal due to the nitro reduction was observed showing that all the nitrocompound encapsulated was reduced in the first scan. In successive scans only a relatively stable quasireversible couple RNO-RNHOH was maintained.

Scanning electron microscopy (SEM) images of the GCE modified with 3,5-DNBA encapsulated in MWCNT reveals a very good distribution and packed. In spite of the similar qualitative voltammetric behavior of 3,5-DNBA obtained according to both procedures i.e. covalent attachment and encapsulation, the last one generates considerably largest currents for similar concentrations.

Acknowledgements: To FONDECYT, Grant 1130160 for his support.

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# Efficient Anodic Degradation of Phenol Paired to Improved Cathodic Production of H<sub>2</sub>O<sub>2</sub> at BDD Electrodes

<u>Patricio J. Espinoza-Montero</u>,\*<sup>a,b</sup> Ruben Vasquez-Medrano,<sup>c</sup> Jorge G. Ibanez,<sup>c</sup> and Bernardo A. Frontana-Uribe<sup>b</sup>

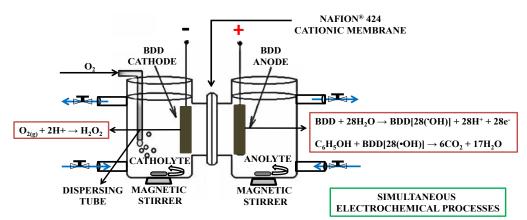
<sup>a</sup>Facultad de Ingeniería Civil y Ambiental, Escuela Politécnica Nacional, Ladrón de Guevara E11-253, C.P.: 170413, Quito, Ecuador, Phone: +593 2 2221306.

<sup>b</sup>Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Carretera Toluca Atlacomulco, 50200 Toluca, Estado de México, México.

<sup>c</sup>Departamento de Ingeniería y Ciencias Químicas, Universidad Iberoamericana, México City 01219 DF,

patoespinozamon@hotmail.com;\*<sup>a,b</sup> patricio.espinoza@epn.edu.ec

Electrochemical degradation of phenol (PhOH) with simultaneous reduction of  $O_2$  to  $H_2O_2$  in acidic media was performed in an H-type divided cell (500 mL), separated with a cationic membrane (Nafion® 424). Boron-doped diamond (BDD) electrodes were used as anode and cathode. The study was divided into three stages: (a) Electroanalytical study of the oxygen reduction reaction (ORR) to  $H_2O_2$  by hydrodynamic linear-sweep voltammetry with a BDD-RDE in acidic and alkaline solutions; (b) galvanostatic ORR to  $H_2O_2$  at BDD electrode in acidic solution (unpaired system); (c) pairing the anodic PhOH degradation with the  $H_2O_2$  cathodic production at BDD electrodes. The best production of  $H_2O_2$ under our conditions with the unpaired system was 250.1 mg L<sup>-1</sup> at 1.5 mA cm<sup>-2</sup> after 540 min of electrolysis; the highest reported to date for BDD electrode in acidic media. Total mineralization of 100 mg L<sup>-1</sup> of PhOH in the paired system required a higher current density (i.e., 2.5 mA cm<sup>-2</sup>); in spite of this, the process is one order of magnitude faster than any electrochemical process previously reported.



Electrochemical H<sub>2</sub>O<sub>2</sub> production and phenol mineralization

# Carbon Nanotubes/Prussian Blue Analogues Thin Films Nanocomposites: Multifunctional Materials

Samantha Husmann, Aldo J. G. Zarbin

<sup>\*</sup>Universidade Federal do Paraná (UFPR) Department of Chesmitry – Av. Cel. Francisco Heráclito dos Santos, n°210, Jd das Américas – Curitiba-PR CEP: 81531-980

samanthahus@gmail.com

Hexacyanometallates (HCM) are a class of compounds with general formula M[M'(CN)<sub>6</sub>], Prussian blue (PB - Fe<sup>III</sup><sub>4</sub>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>3</sub>) being the most studied one. When iron species of PB are substitute for other metals, Prussian blue analogues (PBAs) are obtained. The face-centered cubic structure, electrochromic properties and highly catalytic activity towards H<sub>2</sub>O<sub>2</sub> reduction make the HCM suitable for a large range of applications. Despite these properties, HCM presents low chemical and electrochemical stability, which are a major drawback for their applications. To overcome these problems, PB and its analogues have been applied as composites with different materials, such as carbon nanotubes (CNTs) [1,2]. In our research group, an innovative route for CNT/PB nanocomposites synthesis has been developed [3]. Through a heterogeneous reaction between iron species from CNTs cavities and  $K_3$ [Fe(CN)<sub>6</sub>] aqueous solution, PB is formed directly over CNTs walls by electrodeposition. This route was successfully modified to produce PBAs by changing filler species from CNTs or salts in aqueous solution. By replacing iron species from CNTs cavities for cobalt, cobalt hexacyanoferrate (CoHCFe) were synthesized. In the other way, replacing  $K_3[Fe(CN)_6]$  for  $K_4[Ru(CN)_6]$  originate iron hexacyanoruthenate (FeHCRu), known as ruthenium purple (RP) [4]. Electrodeposition parameters, such pH, showed great influence on morphology and stability of the CNT/PBAs nanocomposites. All nanocomposites were characterized with XRD, Raman and UV-Vis Spectroscopy, SEM and cyclic voltammetry. These nanocomposites showed great stability in electrolytes with different cations, such as K<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup>. Both nanocomposites were applied as H<sub>2</sub>O<sub>2</sub> sensors, showing great analitycal parameters, with limits of detection as low as 1.27 nmol.L<sup>-1</sup> Both CNT/CoHCFe and CNT/RP, along with CNT/PB thin films were also evaluated as batteries material in different electrolytes (K<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup>). CNT/RP films were also applied as electrochromic material, due to its intense purple color and colorless states when oxidized or reduced, respectively. CNT/RP showed great stability and high coloration efficiency, over 95%, maintained during cycles.

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# In-situ electrochemical preparation of graphene electrodes in various ionic liquids and potential electroanalytical applications

Eva Menart<sup>1</sup>, Vasko Jovanovski<sup>1</sup>, Janez Kovač<sup>2</sup>, Samo B. Hočevar<sup>1</sup>, Božidar Ogorevc<sup>1</sup> <sup>1</sup>Analytical Chemistry Laboratory, National Institute of Chemistry Hajdrihova 19, SI-1000 Ljubljana, Slovenia <sup>2</sup> Department of Surface Engineering and Optoelectronics, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia eva.menart@ki.si

Graphene has recently become a widely researched material, both from the point of view of its production and potential application. It has shown promise as an energy storage material (e.g. batteries and capacitors), as a possible replacement for Si in electronics, and as electrode material in sensor development. Graphene has also been suggested as a catalytic material for the oxygen reduction reaction (ORR).

Different approaches to obtaining graphene from graphite have been employed, e.g. micromechanical exfoliation of graphite, chemical vapor deposition, and the most commonly used approach, where graphite is first treated with a strong oxidizing agent to yield nonconductive graphene oxide followed by chemical reduction to conductive graphene (e.g. Hummers method). In addition, different electrochemical approaches for preparation of graphene have been proposed and it has been reported that electrochemical production of graphene sheets provides improved electrical properties and enhanced performance in electrochemical applications compared to chemical oxidation/reduction protocol.

The approach described in this communication differs from the ones described above. Our goal was not to produce graphene sheets and extract them from the electrolyte, but to grow graphene directly (in-situ) onto a graphite electrode, which could then be further used with or without additional modifications, for example, in electroanalytical applications. We significantly upgraded a method [1], where graphite was exposed to a series of voltages in an ionic liquid (IL) as the electrolyte. We used mechanical pencil lead as a non-expensive, simple and widely available precursor material and investigated several ILs with various combinations of cations and anions. This provided different intercalation and functionalization of carbon material. The in-situ prepared graphene electrocatalytic properties. The so prepared electrodes also provided promising results concerning the ORR, thus making the proposed method interesting for a wider range of electroanalytical applications.

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# **Electrochemical Explorations of Graphene and Related Materials**

<u>Craig E. Banks</u>, Manchester Metropolitan University Chester Street, Manchester, M1 5GD, UK c.banks@mmu.ac.uk

Graphene, a planar monolayer of carbon atoms that are densely packed into a 2D honeycomb lattice, has become one of the most intensively explored carbon allotropes in materials science due to its reported unique electronic and mechanical properties. One area that graphene has significantly influenced is in the field of electrochemistry where it is potentially represents the world's thinnest electrode material and has been applied in many areas, such as in sensing and energy storage/conversion.

This talk will explore recent work from my group on graphene and related 2D materials starting with fundamental insights into graphene immobilised upon electrode surfaces via drop coating, Chemical Vapour Deposition grown graphene and 3D freestanding graphene macrostructures. Recent work towards understanding the electrochemistry of graphene will be overviewed.

# Electrochemical and Spectroscopic Studies of Carbon Cathodes for Oxygen Reduction in DMSO Lithium Electrolytes

Ernesto J. Calvo, Santiago Herrera, Florencia Marchini, Nataliia Mozhzhukhina, Walter Torres, Alvaro Tesio, Maria del Pozo Vazquez, F. Williams INQUIMAE-CONICET. DQIAyQF-FCEyN Universidad de Buenos Aires Pabellon 2, Ciudad Universitaria. 1428 Buenos Aires. Argentina

calvo@qi.fcen.uba.ar

The rechargeable Li–air battery exhibits a very large theoretical energy density that can compete with fossil fuels for electric vehicle applications with an extended mileage range. The non-aqueous Li–air battery introduced in 1996 by Abraham consists of a lithium metal anode that dissolves in a non aqueous electrolyte and the resulting  $Li^+$  ions react with oxygen reduction products to form insoluble lithium peroxide  $Li_2O_2$  at a porous carbon cathode during discharge. Among non-aqueous solvents, DMSO with a very large dipole moment and the appropriate geometry to coordinate  $Li^+$  ions stabilizes lithium ion and it has been recently proposed for rechargeable  $Li-O_2$  batteries.<sup>1</sup> However there is a controversy at present on the stability of carbon, DMSO and lithium salts in contact with solid  $Li_2O_2$ .<sup>2-3</sup>

We will present experimental evidence on the surface products of oxygen reduction on carbon electrodes as a function of potential and time during the discharge (ORR) and recharge of the positive electrode in lithium-air batteries.<sup>4-8</sup>

Different carbon materials such as highly oriented pyrolytic graphite (HOPG), glassy carbon and Vulcan carbon black have been investigated with a variety of experimental techniques such as rotating ring-disc electrode (RRDE), differential electrochemical mass spectrometry (DEMS), X-Ray Spectroscopy with an electrochemical transfer system (EC-XPS), electrochemical quartz crystal microbalance (EQCM) and atomic force microscopy (AFM).

EQCM detects co-deposition of DMSO with  $Li_2O_2$  during ORR<sup>6</sup> while AFM has shown the growth of  $Li_2O_2$  at terrace edges of HOPG in the early stages of ORR and RRDE detects soluble lithium superoxide during ORR due to the solvation of  $Li^+$  by DMSO.<sup>8-9</sup>

These studies have shown that while  $L_{12}O_2$  is the main reduction product of oxygen in DMSO lithium electrolyte, a small fraction of that is re-oxidized at 3 V since carbon, DMSO and PF<sub>6</sub> undergo heterogenous decomposition by contact with solid  $L_{12}O_2$  at potentials where ORR occur as shown in XPS experiments. The large overpotential needed to recharge these cathodes is due to oxidation of other species such as organics, carbonates, lithium fluoride, sulfate and phosphorous compounds formed in the presence of surface peroxide. During re-oxidation above 4.3 V, in situ FTIR resuls shows electrochemical oxidation of DMSO to dimethyl sulfone<sup>5</sup>, while DEMS detects formation of CO<sub>2</sub> and consumption of O<sub>2</sub> which reacts with DMSO oxidation intermediates.

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# Synthesis, Characterization and Photoelectrochemical Performance of Hybrid Electrodes Based on Titania Nanotubes and Reduced Graphite Oxide

Monica Cerro-Lopez\*<sup>1</sup>, Abraham Mauleon-Amieva<sup>1</sup>, Alejandra Garcia-Garcia<sup>2</sup>, Yunny Meas-Vong<sup>3</sup>,

Carlos A. Martínez-Huitle<sup>4</sup> and Marco A. Quiroz<sup>1</sup>

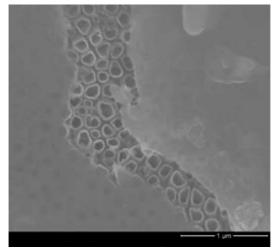
<sup>1</sup>Universidad de las Américas Puebla, Depto. Cs. Químico Biológicas, Lab. de Investigación en Electrocatálisis, Sta. Catarina Mártir s/n, Cholula 72810 Puebla, México. <sup>2</sup>CIMAV Unidad Monterrey, Alianza Norte #202, Parque PIIT, C.P. 66600, Apodaca, Nuevo León, Mexico. <sup>3</sup>Centro de Investigación y Desarrollo en Tecnología en Electroquímica, Parque Tecnológico Querétaro 76703 Sanfandila, Pedro Escobedo Querétaro, México. <sup>4</sup>Universidade Federal do Rio Grande do Norte, Centro de Ciencias Exatas, Depto. Química, Lagoa Nova – Natal 59056-400, RN-Brasil.

e-mail: monica.cerro@udlap.mx

Hybrid electrodes based on titania nanotubes (TiO<sub>2</sub>-Nts) and reduced graphite oxide (RGO) were constructed by electrophoretic deposition of graphite oxide (GO) during the anodization of titanium plates to simultaneously form dioxide nanotubes combined with GO. After anodization, these electrodes (TiO<sub>2</sub>-Nts-GO) were annealed at 500°C during 1.5 hours and then, electrochemically reduced through cyclic voltammetry.

The hybrid electrodes were characterized by FTIR, Raman, and XRD analyses showing that after reduction, the electrode is composed by titanium dioxide in anatase phase, crystalline carbon and reduced graphite oxide (TiO<sub>2</sub>-Nts-RGO). SEM studies showed that layers of RGO are partially covering the nanotubes surface, see Figure 1. I-V curves were obtained under light and dark conditions for the hybrid electrodes (TiO<sub>2</sub>-Nts-GO and TiO<sub>2</sub>-Nts-RGO) in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. I-V curves showed that the highest photocurrent response is obtained with the TiO<sub>2</sub>-Nts-RGO electrode.

The photoelectrochemical performance of these materials was tested for the oxidation (discoloration) of methyl red under constant potential (2V) in acidic aqueous medium. An 80% discoloration of a 15 ppm methyl red solution (50 mL) with a 1 cm<sup>2</sup> electrode was achieved under illumination with a 365 nm light and lamp intensity of 4 mW/cm<sup>2</sup> after two hours of reaction, see Figure 2.



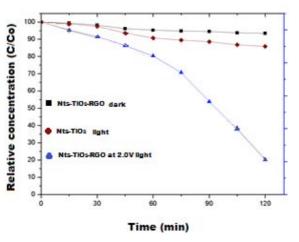


Figure 1. Front SEM image of TiO<sub>2</sub>-Nts-RGO

Figure 2. Comparative MR discoloration

## Carboxylated β-Cyclodextrin-reduced Graphene Oxide for the Voltammetric Determination of Diuron Herbicide

Adriana P. Rodrigues, <u>Ilanna C. Lopes</u>, Thaylan P. Araújo, Sônia Maria C. N. Tanaka, Auro A. Tanaka Universidade Federal do Maranhão - Centro de Ciências Exatas e Tecnologia Avenida dos Portugueses, 1966 – Bacanga, 65080-805 São Luís (MA), Brasil ilannacampelo@hotmail.com

Diuron (DRN), N-(3,4-dichlorophenyl)-N,N-dimethyl-urea, is a water soluble herbicide belonging to the phenylamide and the subclass of phenylurea. This compound has been used to control a wide variety of annual and perennial broadleaf and grassy weeds, as well as mosses [1]. Analytical methods based on electrochemical sensors can be a viable alternative for the monitoring of pollutants in the environment, offering selectivity, sensitivity, low cost, portability, and the possibility of miniaturization [2,3]. The nanomaterials especially the materials based on carbon are employed extensively as sensing materials to detect pollutants owing to their unique chemical, thermal, electronic, and mechanical properties [4]. In this work, a glassy carbon electrode (GCE) modified with carboxylated  $\beta$ -cyclodextrin-reduced graphene oxide (CB- $\beta$ -CD-OGR) for determination of DRN, using cyclic voltammetry (VC), was studied.

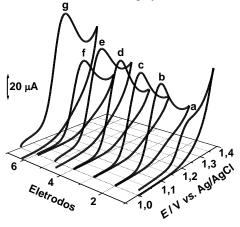


Figura 1. Cyclic voltammograms of DRN 4,5 x  $10^4$  mol L<sup>-1</sup> in pH 1,0 KCl/HCl 0,2 mol L<sup>-1</sup> buffer solution at: GCE (a), GCE/OG (b), GCE/CD- $\beta$ -OG (c), GCE/CB- $\beta$ -CD-OG (d), GCE/OGR (e), GCE/CD- $\beta$ -OGR (f) and GCE/CB- $\beta$ -CD-OGR (g) , v = 50 mV s<sup>-1</sup>.

The oxidation of DRN at GCE is an irreversible, diffusion-controlled, and pH-independent process that occurs with the transfer of only one electron and does not involve the formation of any electroactive oxidation product. After modification of the GCE with hybrids, the results presented in Fig. 1 point out clearly that the voltammetric responses obtained for DRN oxidation using the GCE/CB- $\beta$ -CD-OGR presented the greatest current values and the best voltammetric profiles. These results indicate that this sensor has a better electrocatalytic activity for detection of DRN in pure electrolyte and because of this it will be employed for development of an electroanalytical procedure for determination of DRN in natural water. After optimization of the experimental and voltammetric parameters, calibration curves were obtained for DRN in an electrolyte prepared with pure water, using VC. The responses were recorded for a range of concentration from 1,3 x 10<sup>-8</sup> to 7,9 x 10<sup>-7</sup> mol L<sup>-1</sup>, according to the following equation:  $\Delta I/\mu A = (2,7 \pm 0,6) \times 10^{-7} + (3,3 \pm 0,2) [DRN]/mol L<sup>-1</sup>, with R = 0,9919$  to N = 10 and SD = 1,25 x 10<sup>-7</sup>. Os LD = 2,6 x 10<sup>-7</sup> (59,4 µg L<sup>-1</sup>) e LQ = 8,5 x 10<sup>-7</sup> mol L<sup>-1</sup> (198,1 µg L<sup>-1</sup>) was determined.

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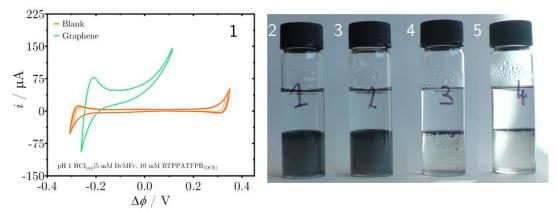
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## Interfacial Adsorption and Catalysis using few-layer Graphene

<u>Andrew N.J. Rodgers</u>, Robert A.W. Dryfe School of Chemistry, University of Manchester Oxford Road Manchester, M13 9PL, UK andrew.rodgers@manchester.ac.uk

The interface between two immiscible electrolyte solutions (ITIES) has increasingly been used for the biphasic reduction of both  $H^+$  and  $O_2$  to  $H_2$  and  $H_2O_2/H_2O$ , in the hydrogen evolution (HER) and oxygen reduction (ORR) reactions, respectively [1]. A wide variety of catalysts, many adsorbed at the ITIES, have been used for both reactions, with carbon-based materials as supports.



CVs recorded on a pH1 HCl<sub>(aq)</sub>|5 mM DcMFc, 10 mM BTPPATFPB<sub>(DCE)</sub> liquid|liquid system, showing the catalytic effect of the few-layer graphene. Biphasic H<sub>2</sub>O|DCE systems, with graphite initially exfoliated and dispersed in the DCE phase, after 15 minute sonication. 2) H<sub>2</sub>O|DCE, 3) 0.1 M LiCl<sub>(aq)</sub>|DCE, 4) H<sub>2</sub>O|10 mM BTPPATPBCl<sub>(DCE)</sub>, 5) 0.1 M LiCl<sub>(aq)</sub>|10 mM BTPPATPBCl<sub>(DCE)</sub>. DcMFc = decamethylferrocene, DCE = 1,2-dichloroethane, BTPPATFPB =

Bis(triphenylphosphoranylidene)ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, BTPPATPBCl = bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl)borate

Herein, we present a study on the use of interfacially assembled few-layer graphene as a catalyst for the ORR, with a view to resolving the homo- or hetero-geneous nature of the reaction mechanism. An important preliminary component to this work involved studying the stability of the graphitic dispersions in the bi-phasic system. The presence of electrolyte in the organic phase vastly improved the interfacial assembly of the few-layer graphene (samples 4 and 5 in the figure above), resulting in an irreversibly attached film. The effects of electrolyte on dispersion stability in <u>organic</u> phases, a hitherto neglected area [2], will also be reported here.

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# Studying the effect of sp<sup>3</sup>/sp<sup>2</sup> ratio on electrochemical oxidation and production of oxidant species using boron doped diamond films

Chrystiane do Nascimento Brito<sup>1</sup>, Danyelle M. de Araújo<sup>1</sup>, Manuel A. Rodrigo<sup>2</sup>, Djalma R. da Silva<sup>1</sup>, Carlos A. Martínez-Huitle<sup>1,\*</sup>.

<sup>1</sup> Institute of Chemistry, Federal University of Rio Grande do Norte, Campus Universitario, Lagoa Nova, Natal, RN, Brazil.
<sup>2</sup>Department of Chemical Engineering, Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain carolaraujo.ufrn@yahoo.com.br

Some authors have questioned the non-active nature of BDD material as well as the reactivity of hydroxyl radicals [1,2] because some results have demonstrated the occurrence of partial oxidation or complete mineralization of organic pollutants when BDD is used as anode. In this point, it seems reasonable to think that the electrochemical process can be greatly affected by the characteristic of the BDD electrodes used. Therefore, few works have showed that the conductive layer characteristics  $(sp^3/sp^2 ratio, boron content, the thickness of the BDD layer) and the substrate properties (resistivity and roughness of the surface) have an important influence in the bulk electrolysis results [3-5].$ 

Nevertheless, recent studies have been proved that the electrochemical combustion or conversion at BDD anodes is strongly related to the active or non-active surface of BDD anodes due to the relation of  $sp^3/sp^2$  [5,6]. In this frame, it seems also reasonable to extend this behavior for the production of strong oxidants on BDD surface. However, these assumptions were not completely verified because no quantification of strong oxidants was performed using BDD anodes with significant differences on the  $sp^3/sp^2$  ratio. Thus, the aim of this work was to present important evidences about the influence of  $sp^3/sp^2$  ratio on the electrochemical oxidation of organic pollutants as well as the production of oxidant species, using BDD samples with distinct diamond content on their surfaces, supplied by one of the more important diamond-electrodes manufacturers.

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## **Carbon Nanotubes for Novel Electrochemical Sensing Applications**

Christopher M.A. Brett, M.M. Barsan, M.E. Ghica, C. Gouveia Caridade

Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra

3004-535 Coimbra, Portugal

## cbrett@ci.uc.pt

Carbon nanotubes have found increasing applications in electrochemistry from fuel cells through to sensors owing to the possibilities afforded by the increased surface area and by electrocatalytic effects. This contribution will focus on the benefits that can be found in electrochemical sensors and biosensors by the use of multiwalled carbon nanotubes (MWCNT) either by themselves or in combination with redox or conducting polymers, where synergistic effects can appear. Electrocatalysis of the desired analytical species and the reduction of interferences are possible together with reduced response time and increased reliability in controlled nanostructures. The source of the MWCNT as well as functionalisation can play an important role [1] as can  $\pi$ - $\pi$  stacking interactions, to complement interactions with functional groups. Examples will be given from recent research, highlighting the voltammetric, electrochemical impedance and surface analysis characterization techniques, as well as application to sensing.

Some examples involve modification of carbon electrodes by MWCNT followed by enzyme immobilisation in an enzyme-containing layer to give an enzyme biosensor. The first is a hypoxanthine biosensor using xanthine oxidase in which the enzyme mechanism of action is shown to involve competition between regeneration of flavin adenine dinucleotide (FAD) and reduction of hydrogen peroxide on the MWCNT [2]. The second is a lipase biosensor that was developed for olive oil triglycerides at an MWCNT-ionic liquid modified glassy carbon electrode [3]. Nitrogen-doped MWCNT were demonstrated to give a superior performance to MWCNT when mixed with PEDOT on carbon cloth electrode substrates [4].

Formation of redox polymers by electropolymerisation on an electrode substrate either before or after MWCNT deposition can lead to interesting sensor films for hydrogen peroxide sensing, e.g. poly(brilliant green) (PBG) with MWCNT [5] and for measurement of pharmaceuticals at poly(Nile blue/MWCNT) [6]. PBG and poly(thionine) (PTH) with MWCNT can be used for sensing and biosensing applications, such as for glucose and uric acid biosensors containing MWCNT and PBG or PTH [7]. The importance of diffusion of monomers through the MWCNT network during electropolymerisation will be addressed.

The further addition of a conducting polymer can increase the physical robustness of the sensor platform and increase conductivity of the modifier film. Thus excellent sensor films for hydrogen peroxide with poly(methylene blue), MWCNT and poly(3,4-ethylenedioxythiophene) (PEDOT), can be constructed, as seen in a cholesterol biosensor [8].

A short comparison with graphene will be made, with a view to demonstrating situations in which MWCNT can have a significant influence on electroanalytical performance. Future trends will be indicated.

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## Electrochemical (bio)sensors based on the use of carbon nanomaterials

<u>Gustavo A. Rivas</u>, Fabiana Gutierrez, Emiliano Primo, Aurelien Gasnier, Marcos Eguílaz, Alejandro Gutiérrez, Guillermina L. Luque, María L. Pedano, Marcela Rodríguez, Nancy F. Ferreyra, María D. Rubianes

INFIQC, Departamento de Físicoquimica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba. Argentina grivas@fcq.unc.edu.ar

This presentation is focused on the discussion of new strategies for the design of (bio)electroanalytical platforms devoted to the sensitive and selective quantification of biomarkers based on the use of carbon nanomaterials. Special attention will be given to the critical selection of the molecules used to functionalize the carbon nanostructures in order to obtain nanomaterials with biorecognition, preconcentration or electrical properties that make possible the efficient sensing of important bioanalytes. We discuss the advantages of electrochemical (bio)sensors obtained by modification of glassy carbon electrodes (GCE) with multiwalled carbon nanotubes (MWCNT) non-covalently functionalized by dispersion in polyhistidine (Polyhis), calf-thymus double stranded DNA (dsDNA), and polylysine (Plys).

The dispersions were obtained by mixing the MWCNT with the given polymer (prepared in 50% ethanol solution) followed by sonication for a given time. The (bio)sensors were obtained by drop-coating on polished GCE and further evaporation of the solvent at room temperature. The resulting electrodes (GCE/CNT-polymer) were used for (bio)sensing of : I) the hybridization event using GCE/CNT-Plys taking the system oligo(dG)-oligo(dC) as model; II) glucose using GCE/CNT-polymer modified by self-assembling of glucose oxidase (GOx); III) Cu(II) using GCE/CNT-Polyhis; IV)promethazine using GCE/MWCNT-dsDNA. The modification of GCE with SWCNTs covalently functionalized with Polylys, lysine, tyrosine, and cysteine was also investigated to obtain analytical platforms for the quantification of glucose, dopamine and heavy metals, respectively.

Chemically reduced graphene oxide obtained from the oxidation of graphite and graphene nanoribons obtained from the oxidation of MWCNTs were also used for the construction of (bio)sensing electrochemical platforms. The reduced graphene oxide (RGO) was incorporated in a composite material containing graphite and mineral oil and the resulting electrode was used for the successful quantification of NADH and Do in the presence of ascorbic acid. The usefulness of graphene nanoribons was also demonstrated in connection with the highly successful quantification of dopamine either in solution or by adsorptive stripping with differential pulse voltammetry transduction and medium exchange.

In summary, the proposed (bio)sensors demonstrate that the judicious and intimate coupling of a suitable (bio)molecule and an electrochemical transducer efficiently modified with carbon nanomaterials makes possible the development of highly sensitive and selective bioanalytical devices.

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## Development of C - TiO<sub>2</sub> electrodes obtained by compression

<u>Neemias Cintra Fernandes</u><sup>1,2</sup>, Luane Ferreira Garcia<sup>2</sup>, Jerônimo Raimundo de Oliveira Neto<sup>2</sup>, Fernando Miguel de Amorim Lino<sup>2</sup>, Eric de Souza Gil<sup>2</sup>.

<sup>1</sup> Department of Chemistry, Federal Institute of Goiás. Rua 75, 46 - Setor Central, 74055-110, Goiânia-GO, Brazil.

<sup>2</sup> Faculty of Pharmacy, Federal University of Goiás. Av. Universitária, s/n, 74605-220, Goiânia-GO,

Brazil

E-mail: neemiasfernandes@gmail.com

The electrochemical remediation technology is a viable and promising alternative to perform the mineralization of organic compounds or, at least, to convert persistent organic compounds into more biodegradable species [1, 2, 3, 4]. Among the starting materials for electrode construction, carbon derivatives have good conductivity, large potential window, physical and chemical stability, as well as good affinity for organic pollutants and adsorption properties. For instance, electrodes for anodic oxidation should have good physical and chemical stability, i.e. to corrosion, erosion and passivation; good electrical conductivity, high catalytic efficiency and low relative cost [3, 5, 6].

The pharmaceutical technology, specifically the know-how on solid pharmaceutical forms production, may be linked to carbon electrodes development techniques to provide modified solid carbon electrodes able to attend all the physical, chemical and electrochemical requirements related to electrode construction. In this context, the aim of our work was to develop carbon electrodes modified by  $TiO_2$ , and use them as working electrode in heterogeneous photocatalysis and electrochemical remediation of Cathecol (1,2-dihydroxybenzene). The electrodes were obtained by compression of different proportions of carbon and  $TiO_2$  thinly homogenized. The  $TiO_2$ :C proportions used were 0:1; 1:3; 1:5 and 1:10. To assure the uniformity and reproducibility of carbon modified tablets, the control of parameters like resistivity, hardness, weight and thickness were observed.

The percentual decay of Cathecol concentration, measured after heterogeneous photocatalysis and electrochemical remediations using the modified carbon tablets, was taken by means of HPLC. Preliminary studies shows the better results were detected on the bigger concentration of  $TiO_2$  on carbon modified tablets.

Further studies on development of compressed modified carbon electrodes, the operating parameters of the heterogeneous photocatalysis and electrochemical remediations are underway.

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# Synthesis and characterization of α-Fe<sub>2</sub>O<sub>3</sub>/reduce graphene oxide electrodes for application in photoelectrocatalysis.

Vanildo Souza Leão Neto<u>, Luiz Henrique Dall'Antonia</u> Departamento de Química – Universidade Estadual de Londrina Rodovia Celso Garcia Cid, PR 445, Km 380, Cx. Postal 10.011, CEP 86057-970, Londrina-PR luizh@uel.br

The photooxidation of polluting materials has been a major area of research in recent decades. Several techniques have been employed in pursuit of mineralization of these materials. Among these techniques the heterogeneous photocatalysis has been one of the most promising. However photocatalysis has some limitations, among which stands out the process of recombination of electron-hole pairs. An alternative to trying to reduce this recombination is photoelectrocatalysis.<sup>1</sup> Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is a semiconductor that has been for decades considered a promising material for photoelectrocatalysis. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is a n-type semiconductor with energy band-gap of 2.2 eV (visible light region). However its photocatalytic activity is diminished by several factors.<sup>2</sup> Reduce graphene oxide (rGO) has an important role to improve this photocatalytic activity of semiconductors.<sup>3</sup> The synthesized material (rGO,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/rGO) were characterized by several techniques such as XRD, SEM, TG and FTIR and electrochemical characteristics. The electrodes were prepared using the layer by layer technique with 1 up to 4 layers of hematite and a positively charged polyelectrolyte (poly(diallyldimethylammonium chloride, PDDA). The hematite was thermically treated at 750 and 900 °C. The electroactive areas (A\*) of all the electrodes were estimated (Table 1). The photoelectrochemical profiles for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/PDDA electrodes showed an augmentation in photocurrent when potential shifts for more positive values, characteristic of n-type semiconductor. Moreover, photocurrent density drops close to zero when the light is cut off from the electrodes surface showing a very fast mechanism. The variation of current from dark to lightly exposed surface ( $\Delta_i$ ) for different electrodes are showed in Table 1 The photoelectroactivity of these synthesized materials were tested by methylene blue discoloration. The color diminution follows the pseudo-first order kinects, in studied photoelectrodes under visible light irradiation. All electrodes synthesized with the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/PDDA 900 °C presents better results than the material calcined at 750 °C, probably due a more crystalline material once the active area has not a pronounced increase. With the aim of improvement in the dispatch of the catalytic in photoelectrodes the positively charged polyelectrolyte layers was substituted by rGO forming a bilayer  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 900 °C/rGO with two different terminations: one with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 900 °C and another with rGO. These electrodes presents higher values of photocurrent, rate constants and dye discoloration when compared with electrodes  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 900 °C/PDDA, Table 1 The results show how important is the rGO as a conductivity material present in the film. The synergic effect between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> 900 °C and rGO was evidenced in this study. The dye discoloration in photocatalysis was found to be around 23 and 32% for hematite treated at 750 and 900 °C, respectively. This shows that the junction of electrochemical and photochemical techniques improve the efficiency of a catalytic material. This is due to the motion of the excited electron from the semiconductor to be transported to the counter electrode, in this way the hole generated form radicals OH• to oxidize organic molecules more effectively.

**Table 1.** Variation of current density ( $\Delta j$ ) obtained for electrodes synthesized with differentes layers at +1.3 V (Na<sub>2</sub>SO<sub>4</sub> 0.1M) with and without irradiation of visible light, electroactive area (A\*), the rate constant ( $k_{obs}$ ) of degradation of the dye and percent discoloration of methylene blue at +1.1 V.

Electrode	Δj /	A* /	$k_{obs}/(x10^{-3}min^{-1})$	$\mathbb{R}^2$	% discol.
(layers/materials)	$(\mu A/cm^2)$	$(cm^2)$			
1/α-Fe <sub>2</sub> O <sub>3</sub> /PDDA 750°C	0.03	1.03	3.45	0.926	34
4/ α-Fe <sub>2</sub> O <sub>3</sub> /PDDA 750°C	0.03	1.34	6.84	0.994	54
1/α-Fe <sub>2</sub> O <sub>3</sub> /PDDA 900 °C	0.04	1.15	4.08	0.995	39
4/α-Fe <sub>2</sub> O <sub>3</sub> /PDDA 900 °C	0.21	1.28	6.85	0.994	56
4/ α-Fe <sub>2</sub> O <sub>3</sub> 900 °C/rGO	1.56	1.21	8.91	0.994	63
4/ rGO/α-Fe <sub>2</sub> O <sub>3</sub> 900 °C	2.15	1.31	11,90	0.976	78

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# Functionalization of Graphite in Friedel-Crafts Reaction Condition: Electrochemical Characterization and Aging.

David T. A. Sawazaki<sup>1</sup>, Edgar T. Suzuki, Zeki Naal<sup>2</sup>

<sup>1</sup>Department of Chemistry - Faculty of Philosophy Science and Letters of Ribeirao Preto Av. Bandeirantes, 3900 - CEP 14040-901 - Bairro Monte Alegre - Ribeirão Preto - SP-Brazil. <sup>2</sup> School of Pharmaceutical Sciences at Ribeirão Preto, SP, Brazil. david.sawazaki@usp.br; zekinaal@usp.br

## Introduction

The use of graphitic materials on amperometric sensing and electronic devices resides in their conductivity. The functionalization of these materials aiming a better analytical signal may lead to a loss of conductivity due to the break of unsaturated bonds. In this way, the development of controlled functionalization conditions is an important step to obtain electrode materials with appropriate properties. Furthermore, the aging process that occurs in the material may be used as a post-synthesis treatment to enhance its performance.

## **Materials and Methods**

The graphite used was from Fisher Chemicals, and the Ferrocenemonocarboxylic acid (FCA) and Aluminum Chloride was from Sigma-Aldrich. The synthesis was carried out in a microwave reactor DISCOVER benchmate from CEM at different radiation powers. The working electrode was a Carbon Paste Electrode (CPE) with a geometric area of 0.054 cm<sup>2</sup>. The mineral oil (nujol) used was Sigma-Aldrich. The reference electrode was Ag/AgCl and the counter electrode was a Pt wire.

#### Results

The reaction was carried out at three radiation powers: 10W, 20W and 40W. The extent of functionalization increased with the power. At higher radiation power, the material presented less conductivity, as can be seen in Figure 1a. However, after one year at room temperature, the same material presented a voltammetric profile as can be seen at figure 1b. Based on the mechanism suggested, the conductivity was restored due to a rearranging of oxygen groups in the material with subsequent oxygen or water formation<sup>1,2</sup>. Our results showed that the reaction does not occur neither when the material is dried nor in the absence of AlCl<sub>3</sub>. The FTIR results show a band at 1650cm<sup>-1</sup> in the FCA and physical mixture spectra, but at 1580cm<sup>-1</sup> after the reaction (ketone near aromatic system). Raman and thermal analyses corroborates the functionalization of graphite.



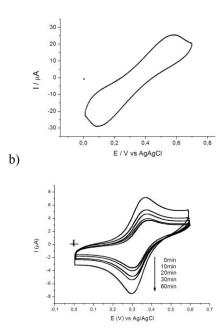


Figure 1: Cyclic voltammograms of Graphite-FCA functionalized at 40W. a) newly synthetized b) one year after at room temperature. Phosphate Buffer 0.1M pH = 7.0,  $0.1Vs^{-1}$ .

### Conclusion

In this work we presented a microwave assisted functionalization of graphite in Friedel-Crafts conditions. The results suggest a reaction mechanism dependent on the moisture of the material and on the microwave radiation power. An aging process seems to occur and reestablish the conductivity of the material.

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# Layer-by-Layer Electrochemical Fabrication of Reduced Graphene Oxide-Metal/Metal Oxide Nanocomposites for Catalyst and Sensor Applications

## <u>Ümit Demir</u>, Tuba Öznülüer, Hülya Öztürk Doğan Department of Chemistry, Faculty of Sciences, Atatürk University, Erzurum, Turkey 25240 udemir@atauni.edu.tr

Graphene-based materials show great potential for application in energy storage, solar cells, heterogeneous catalysis, sensors etc. Therefore, the researchers have been studied on the new methods that improve the chemical/physical properties of graphene and make it more functional for various applications. Incorporation of different materials into the graphene is a promising way to synthesize hybrid composites with novel properties [1]. Especially, the hybrid composites that are formed by the anchoring of metal or metal oxide with graphene or GO have been the most studied research topic in the recent years. However, those composites were generally prepared by chemical methods and in the form of three-dimensional nanoparticles.

In this work, we have presented a novel and simple strategy to fabricate layered reduced graphene oxide (ERGO)-metal (Cu, Pd) nanocomposites by using electrochemical reduction of GO and underpotential deposition (UPD) of Cu and Pd monolayers. The presented UPD-based electrochemical method [2] which provides two-dimensional atomic-layer growth of metal layers has not been reported yet in the literature. Here, a single atomic layer of Cu or Pd metals has been deposited electrochemically on the surface of Au or indium tin oxide (ITO) electrode by UPD technique. Then GO has been reduced electrochemically on top of these metallic monolayers in order to form one layer of Cu-ERGO or Pd-ERGO nanocomposites [3]. The thicker (-Cu-ERGO-)<sub>n</sub> or (-Pd-ERGO-)<sub>n</sub> sandwich-structured composites can be electrodeposited by repeating the sequential UPD and electrochemical reduction of GO. The ERGO-metal oxide nanocomposites were obtained by the oxidation of deposited metallic monolayer when the UPD deposition was performed in the presence of dissolved O<sub>2</sub> [4].

Our results indicated that the ERGO-based metal/metal oxide composites could be prepared directly on the electrode surface without the need for more processes for the electroanalytical applications. Moreover, composites that have the desired composition, structure and properties could be easily prepared by the layer-by-layer manner by changing the electrochemical parameters. X-ray diffraction (XRD), Raman Spectroscopy, X-photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), scanning tunneling microscopy (STM) and scanning electron microscopy (SEM) techniques were used to characterize the ERGO-based metal composites. Electrochemical and photocurrent measurements revealed that those composites are promising candidates for the catalysis and sensor applications.

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## **Electron Transfer Kinetics on Graphene**

<u>Matěj Velický</u>, Robert A.W. Dryfe School of Chemistry, University of Manchester Oxford Road, Manchester, M13 9PL, United Kingdom matej.velicky@manchester.ac.uk

The unique properties of the two-dimensional crystal of carbon, graphene, have sparked an enormous research interest to explore its electrochemical properties, with potential applications in sensing, corrosion protection, and energy conversion/storage. Understanding how the electron transfer kinetics of a redox reaction between the surface of graphene and a molecule compare to bulk graphite is crucial to the future use of graphene as a high-performing electrode material. Nevertheless, despite the significant research efforts in the recent years, the fundamental electron transfer behavior on graphene is not fully understood, which demonstrated by the large discrepancies between findings originating from different groups.[1-3]

Herein, the electrochemical response of high-quality, mechanically exfoliated graphene/graphite electrodes is evaluated using a micro-droplet cell (see Fig.1), which allows the pristine basal planes, edges planes/defects and *in situ* cleaved surfaces to be accessed separately.[4] Contrary to previous views, the basal planes of both graphene and graphite are electrochemical active, and although the number of graphene layers has some effects on electrochemical response, there is no significant difference between

electron transfer kinetics on graphene monolayer and bulk graphite. Heterogeneous electron transfer rate  $(k^0)$  measurement of known redox mediators reveal that local surface conditions on graphene surface have a significant effect on the electrochemical activity, which explains the vast variation of  $k^0$  values in literature. Furthermore, although little difference in electrode kinetics is seen between the pristine and defective basal planes of graphite, significant increase in kinetics on *in situ* cleaved surfaces is observed. These differences attributed to the modification of the surface by airborne contaminants as determined by X-ray photoelectron spectroscopy and energydispersive X-ray spectroscopy.[5]



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## Impedance Characterization of Multiwalled Carbon Nanotubes-Polymer based Flexible Thin Film Piezoresistive Strain Sensors

<u>A. Sanli</u>, A. Benchirouf, A. D. Thakur, C. Müller, O. Kanoun Technische Universität Chemnitz, Chair of Measurement and Sensor Technology Reichenhainer Straße 70, 09126 Chemnitz, Germany abdulkadir.sanli@s2012.tu-chemnitz.de

Since their discovery by Iijima in 1991 [1], carbon nanotubes (CNTs) have been intensively studied for decades and they have attracted a great attention owing to their superior mechanical and physical properties. For the realization of the potential of CNTs based strain sensors, numerous approaches are illustrated in the form of CNTs films as buckypapers [2-4] and CNTs/polymer composites [5-7]. However, CNTs bukypapers strain sensors have many drawbacks in terms of fragility and weakness in stress transfer since the CNTs are bonded only by van der Waals forces [8]. To overcome these limitations, appropriate fabrication process, polymer and substrate choice are needed. In this work, thin film piezoresistive strain sensors based on multi-walled carbon nanotubes (MWCNTs)-epoxy nanocomposites with MWCNTs content ranging from 0.25 wt. % to 1 wt. % were prepared by direct mixing method and the final composites were deposited on a flexible thin polyimide substrate (Kapton HN) by screen printing. The dispersion quality and the homogeneity of the nanocomposites at different MWCNTs concentrations were analyzed by electron microscopy and atomic force microscopy. Furthermore, the effects of the processing parameters such as; MWCNTs concentration, sonication and curing on the electrical properties and the piezoresistivity of thin films were investigated quantitatively by electrochemical impedance spectroscopy (EIS) over a wide range of frequency from 40 Hz to 10 MHz. From the impedance characterization of thin films, it was found that the transition from the insulator-toconductor took place between 0.25 wt. % and 0.3 wt. % of MWCNTs content. Moreover, in order to estimate the relative change in the complex resistor-capacitor (RC) network of the strain sensors, an equivalent RC model was proposed and relative changes in the corresponding parameters under strain were extracted by adapting the stochastic algorithms [9]. Consequently, in order to confirm the reliability of strain sensors over time, physical aging of the thin film strain sensors is also investigated by EIS.

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# Nanostructured Conductive Anion Exchange (TPQPOH) Ultra-Thin Langmuir-Schaefer films for Electrocatalytic Application

Paolo Bertoncello<sup>1</sup>, Thomas Jones<sup>1</sup>, Delia Puzzovio<sup>1</sup>, Marialilia Pea<sup>2</sup>, Andrea Notargiacomo<sup>2</sup>, Robert Kaspar<sup>3</sup>, Michael Letterio<sup>3</sup>, and Yushan Yan<sup>3</sup>

<sup>1</sup>College of Engineering, Swansea University, Swansea SA2 8PP, United Kingdom <sup>2</sup>CNR, Institute of Photonics and Nanotechnology, 00156 Rome, Italy <sup>3</sup>Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA

## p.bertoncello@swansea.ac.uk

We report for the first time, the fabrication of Langmuir-Schaefer (LS) films of a soluble and highly conductive quaternary phosphonium-based ionomer (TPQPOH) deposited on boron-doped diamond electrodes (BDDEs) and glassy carbon electrodes (GCEs). The Langmuir-Schaefer is a precise, versatile and relatively simple method, which allows the formation of highly ordered molecular architectures with the advantage of controlling the thicknesses up to the molecular level. First, TPQPOH ionomer was synthesized following the procedure developed by Yan et al. [1]. Then, TPQPOH ultra-thin films were fabricated by using the Langmuir-Schafer method developed by Bertoncello et al. for Nafion [2]. The effect of ionomer concentration, subphase electrolyte concentration, and surface pressure was thoroughly investigated. The pressure-area isotherms showed a behavior strongly dependent upon the subphase (e.g., deionised water, NaCl, and HCl solutions) utilised for the deposition of the LS films. TPQPOH ultra-thin LS films were characterized using a variety of microscopic (Atomic Force Microscopy, AFM and Surface Enhanced Ellipsometric Contrast, SEEC), spectroscopic (UV-visible and Fourier Transform Infrared, FTIR) and electrochemical (cyclic voltammetry, CV and cyclic amperometry, CA) techniques. Interestingly, CV showed the effectiveness of TPQPOH on preconcentrating anionic redox probes, such as  $K_4$ Fe[CN]<sub>6</sub>,  $K_3$ Fe[CN]<sub>6</sub> and  $K_2$ IrCl<sub>6</sub>, and permselectivity by repelling positive charged redox mediators. The electrochemical performances were compared with those obtained using recasted TPOPOH films. These novel TPQPOH ultra-thin LS films were tested towards electrocatalytic sensing of negatively charged species such as ascorbic and uric acids, as model analytes.

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# Use of Electrochemically Pretreated Boron-Doped Diamond Electrodes in Electroanalytical Methods

#### Orlando Fatibello-Filho

# Dep. of Chemistry, Universidade Federal de São Carlos, C.P. 676, 13560-970 São Carlos – SP, Brazil bello@ufscar.br

Electroanalytical methods offer in most cases the possibility of determining the concentration of an analyte directly in the sample of interest, without any sophisticated pretreatment or chemical separation, as well as of analyzing colored materials and samples with dispersed solid particles. Moreover, they offer the possibility of the simultaneous and fast determination of several target analytes with high sensitivity and low cost. On the other hand, boron-doped diamond (BDD) films have proved to be excellent electrode materials for several electroanalytical applications, due to their outstanding properties, which are significantly different from those of other conventional electrodes, *e.g.* glassycarbon, gold or platinum electrodes The electrochemical behavior of BDD electrodes depends on their physical, chemical, and electronic properties, which can be significantly affected by the surface termination such as hydrogen, oxygen, and others. Specifically, the enhancement of hydrogen terminations (HT-BDD) or oxygen terminations (OT-BDD) may be attained by electrochemical methods involving hydrogen evolution or oxygen evolution, respectively. HT-BDD commonly presents relatively high electron transfer rates, compared to OT-BDD, as pointed out, *e.g.*, by Suffredini *et al.* [1] and extensively reviewed by Andrade *et al.* [2]; however, this behavior is quite dependent on the species being oxidized or reduced, as will be presented in this lecture.

In the last years, BDD electrodes have been used in our research group in the development of several electroanalytical methods for sundry analytes, solely or simultaneously with others. For this task, during the development of each analytical method, the effect of electrochemical pretreatments (cathodic or anodic) on the response of the BDD electrode was investigated. Thus, in this presentation the effect of anodic and cathodic electrochemical pretreatments on the electrochemical response of some redox couples will be comparatively discussed. In addition, the electrochemical applications of cathodically pretreated BDD electrodes in the determination of several analytes in different matrixes such as biological, food, and pharmaceutical products will be presented.

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# Electrochemical Communication between Bacterial Cells/Biological Membranes and Carbon Electrodes

Lo Gorton<sup>1</sup>, Kamrul Hasan<sup>1</sup>, Dónal Leech<sup>3</sup>, Cecilia Hägerhäll<sup>1</sup>, Sinan Cem Emek<sup>1</sup>, Per-Åke Albertsson<sup>1</sup>, Hans-Erik Åkerlund<sup>1</sup>, Yusuf Dilgin<sup>4</sup>, Michael A. Packer<sup>5</sup>, Eva Sperling<sup>1</sup>, Peter ÓConghaile<sup>3</sup>, Huseyin Bekir Yildiz

<sup>1</sup> Lund University, P.O.Box 124, SE-221 00 Lund, Sweden, <sup>2</sup> Ghent University, Belgium. <sup>3</sup> National University of Ireland Galway, Ireland, <sup>4</sup> Çanakkale Onsekiz Mart University, Çanakkale, Turkey, <sup>5</sup>Cawthron Institute, 98 Halifax Street, Nelson, New Zealand, <sup>6</sup> Department of Materials Science and Nanotechnology Engineering, KTO Karatay University, 42020 Konya, Turkey Lo.Gorton@biochemistry.lu.se

Electrochemical transfer (ET) communication between bacterial cells and electrodes can usually be obtained through the use of freely diffusing monomeric redox mediators. Previously we have, however, also shown that flexible osmium redox polymers can work as efficient mediators for a number of both Gram – as well as Gram + bacteria and electrodes, clearly showing that the mediator does not need to pass the inner membrane to be able to shuttle the charge between the cells and the electrode [1]. In some restricted cases ET can be obtained directly between the bacterial cells and the electrode, e.g. between Geobacter sp. and Shewanella sp. and various carbon electrodes [2,3]. Here it will be shown that the current density from Shewanella oneidensis MR-1 to graphite electrodes in the presence of lactate can be increased at least four times by the use of an Os-polymer with an  $E^{\circ}$ value of 0.221 V (vs Ag|AgCl, sat. KCl) compared with the use of naked graphite [4]. Further increases in the current density for bioelectrocatalysis can be obtained by exchanging ordinary graphite electrodes for electrospun carbon fibres. For example for 18 mM lactate the current density increased from 10 to 120 µA/cm<sup>2</sup> [5]. Currently we are also investigating the effect of feeding the cells with cis-platin, which causes the cells just to grow but not to divide. When comparing normal cells with cis-platin treated cells it is possible to get current densities up to six times higher with the treated cells [6]. We have now extended our studies to include photosynthetic organisms/membranes. Successful electrochemical communication between isolated photosystem I and II and electrodes have been known for some time [7,8] however, here we report on electrochemical communication between whole viable photosynthetic bacterial cells (*Rhodobacter capsulatus* [9, 10] and *Leptolyngbia* sp [11].) as well as with eukaryote systems (thylakoid membranes from spinach [12], the eukaryote unicellar algae *Paulschulzia pseudovolvox*) and electrodes through the use of osmium redox polymers.

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# Inhibition of chlorate and perchlorate formation during clofibric acid degradation by electro-peroxone process

Zhirong Lin, Shi Yuan, Huijiao Wang, Xiang Li, Yujue Wang\*

State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment,

Tsinghua University, Beijing 100084, China

## wangyujue@tsinghua.edu.cn

Formation of chlorate (ClO<sub>3</sub><sup>-</sup>) and perchlorate (ClO<sub>4</sub><sup>-</sup>) from chloride (Cl<sup>-</sup>) is a major barrier for the wide application of electrolysis technology in water and wastewater treatment. Recently, it has been shown that formation of ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> can be inhibited when H<sub>2</sub>O<sub>2</sub> is simultaneously produced from sparged O<sub>2</sub> during electrolysis process (referred as electrolysis-H<sub>2</sub>O<sub>2</sub> hereafter) because H<sub>2</sub>O<sub>2</sub> can reduce the precursors of ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> (e.g., ClO<sup>-</sup> and ClO<sub>3</sub><sup>-</sup>) back to Cl<sup>-</sup> and ClO<sub>2</sub> [1]. However, the electrogenerated H<sub>2</sub>O<sub>2</sub> may negatively affect pollutant mineralization because H<sub>2</sub>O<sub>2</sub> can consume •OH generated at the anode surface (as shown in Fig. 1(a)). To inhibit ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> formation while still obtaining satisfactory pollutant degradation efficiency, we proposed to adapt the electrolysis-H<sub>2</sub>O<sub>2</sub> process to electro-peroxone (E-peroxone) process, which is an emerging electrochemical advanced oxidation technology and has shown great potentiality in water and wastewater treatment [2].

The E-peroxone process combines conventional electrolysis with ozonation process, and uses a carbon-based cathode to electrochemically produce  $H_2O_2$  from  $O_2$  in the sparged ozone generator effluent ( $O_2$  and  $O_3$  gas mixture) [2]. The in-situ generated  $H_2O_2$  then react with sparged  $O_3$  to produce powerful •OH oxidant. Thus, we expected that by optimizing the rate of  $H_2O_2$  electro-generation, the E-peroxone process may be able to control  $ClO_3^-$  and  $ClO_4^-$  formation and enhance pollutant mineralization simultaneously. To test this hypothesis, we investigated degradation of clofibric acid by electrolysis, electrolysis- $H_2O_2$ , and E-peroxone process. As shown in Fig. 1, while electrolysis using a boron-doped diamond (BDD) anode effectively mineralized clofibric acid, it produced considerable amounts of  $ClO_3^-$  and  $ClO_4^-$ . Although the electrolysis- $H_2O_2$  decreased  $ClO_3^-$  and  $ClO_4^-$  formation by ~30%, it decreased TOC elimination efficiency considerably. In comparison, the E-peroxone process using a Pt/Ti anode can effectively inhibit  $ClO_3^-$  and  $ClO_4^-$  formation while still obtain satisfactory TOC elimination. Based on this promising preliminary result, we are conducting further study to optimize the E-peroxone process for pollutant mineralization and  $ClO_4^-$  control. Recent progress will be reported.

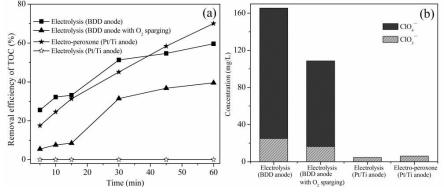


Fig. 1. (a) TOC removal and (b) ClO<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> formation during clofibric acid degradation by electrolysis, electrolysis-H<sub>2</sub>O<sub>2</sub>, and E-peroxone process (carbon-PTFE as the cathode for all processes).
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# Electrochemical Applications of Conductive Diamond Electrodes and the Tailored Design for the Applications

<u>Takeshi Watanabe</u>, Yasuaki Einaga Department of Chemistry, Keio University, and JST-CREST Hiyoshi, Yokohama, 223-8522 Japan nabeta@chem.keio.ac.jp

Boron-doped diamond (BDD) electrodes are very attractive material, because of their wide potential window, low background current, chemical inertness, and mechanical durability. In these years, we have reported several examples for electrochemical sensor applications. Furthermore, other applications such as organic synthesis, ozone generation, and  $CO_2$  reduction have also been developed. On the other hand, the designing electrode should be regarded as important for the practical applications.

We have aimed at designing the diamond electrodes and their electrode systems for several applications in order to exploit the properties of diamond electrodes.

## Electrode design based on the controlling diffusion for the enhancement of the selectivity in sensors

The one of the main challenges in the developments of electrochemical sensors is selectivity. Real samples such as bloods and environmental water contain various substances including not only target species but also interfering species. To avoid the influence of interfering species, the design of diffusion layer based on the designing configuration of electrodes is an effective approach. In this study, electrode configurations using boron-doped diamond were designed and utilized for implementing the concept of controlling diffusions.

The configuration, consisting of a regular array of nickel microdisks on a BDD electrode substrate, was utilized for non-enzymatic glucose sensors. In this electrode, each nickel microdisk acts as a microelectrode for glucose (hemispherical diffusion) due to the inactive diamond surface for glucose oxidation while interfering species such as ascorbic acid are oxidized at the diamond surface (linear diffusion). The difference in diffusion profiles gives a difference in the time dependence of the amperometric response. Selective glucose detection was achieved by utilizing the different time-dependence between glucose and interfering species.

Another configuration, consisting of a BDD as sensing electrode, a perforated carbon plate as interference-depleting electrode and an insulating rubber gasket sandwiched between both electrodes, was utilized for selective cadmium detection against copper interference. By the pre-electrolysis using perforated carbon, copper-free region was created between both electrodes and therefore, cadmium detections without copper-interference could be performed.

Electrode design based on the concept of controlling diffusion offers a simple and practical method to solve the problem of selectivity.

## Tailoring the properties of BDD electrodes with boron concentration and sp<sup>2</sup>-bonded carbons

Although BDD is a candidate electrode material for various electrochemical applications, each application does not necessarily require the same properties. Consequently, the electrode design appropriate for each application is important. The electrochemical properties of diamond can be substantially affected by the boron doping concentration, surface termination and non-diamond  $sp^2$ -bonded carbon impurities. The sp<sup>2</sup>-bonded carbon impurities are considered to lose the some inherent properties of diamond electrode or perhaps expected to enhance the electrode activity.

We investigated the effect of  $sp^2$ -bonded carbon impurities on the electrochemical properties in moderately boron-doped ([B] <  $10^{20}$  atoms cm<sup>-3</sup>) and heavily boron-doped ([B] >  $10^{21}$  atoms cm<sup>-3</sup>) diamond films. The  $sp^2$ -bonded carbon impurities-contained BDD films were prepared for both boron doping levels. Significant influences of  $sp^2$ -bonded carbon impurities, which show glassy carbon-like electrochemical properties after anodic oxidation, were observed in heavily boron-doped diamond. On the other hand, their durability were still similar to diamond electrodes rather than glassy carbon electrodes because of low fraction of  $sp^2$ -bonded carbon impurities. Such "active" diamond electrodes are much less suitable for wastewater treatment while a much higher efficiency for electrochemical ozone production than the other BDD electrodes. These results suggest the electrode properties of BDD can be tailored for each application by controlling the boron doping level and introducing the  $sp^2$ -bonded carbon impurities.

# Nano-Hydrogel/Carbon Nanotubes Electrodes For Matrix Independent Sensing

<u>Andreas Lesch</u>,<sup>a,#</sup> Fernando Cortés-Salazar,<sup>a</sup> Véronique Amstutz,<sup>a</sup> Philippe Tacchini,<sup>c</sup> Hubert H. Girault<sup>a</sup> <sup>a</sup> Ecole Polytechnique Fédérale de Lausanne, Switzerland <sup>b</sup> Edel for Life, Lausanne, Switzerland <sup>#</sup> andreas.lesch@epfl.ch

Carbon nanotubes (CNTs) based electrodes have found several sensing applications including the electrochemical monitoring of antioxidants (AOs). It has been found that CNT based electrodes show faster kinetics and a catalytic effect compared to conventionally applied carbon paste electrodes.<sup>[1]</sup> However, measuring in complex fluids such as wine and fresh juice samples is challenging due to so-called matrix effects induced by the sample composition that affect significantly the electrode surface and thus the electrode's response.

Herein, we present CNT electrodes covered with a nanometer thin layer of a polyacrylamide (PA) hydrogel that show outstanding improvements for the electrochemical detection of antioxidants in complex matrices thanks to the properties of the CNTs and PA coating. Batches of disposable PA/CNT electrodes were prepared fully by multi-layer inkjet printing (IJP) with high accuracy and reproducibility. Within this process, printed stand-alone CNT electrodes on polyimide are covered with a nanometer thin layer of PA thanks to a novel IJP strategy based on the simultaneously performed UV photopolymerization of a specifically prepared acrylamide/*N*,*N*'-methylenebisacrylamide ("bis") containing ink.<sup>[2]</sup> One key step of this new concept is the pre-polymerization. Both properties are crucial for fast and reproducible IJP of disposable PA-modified CNT electrodes.

The gel coated sensors were optically and electrochemically characterized and their use as amperometric sensors for the direct detection of AOs in untreated red wine and fresh orange juice containing pulp and fibers will be demonstrated in this contribution. Compared to bare CNT and carbon paste electrodes, the hydrogel coating compensates for matrix effects as it is usually only achieved by dilution and/or filtering of the sample.

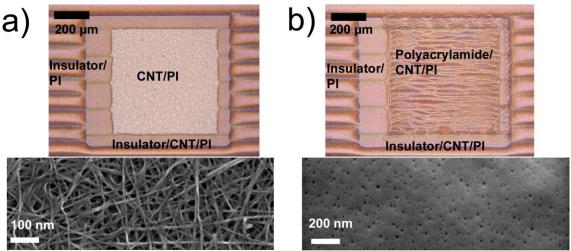


Figure. a) Fully inkjet-printed, stand-alone CNT electrodes and b) nano-polyarylamide/CNT electrodes [2].

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# Electroanalytical Devices Based on Carbon Nanotubes, Reduced Graphene Oxide and Graphene

Lauro Tatsuo Kubota, Murilo Santhiago, Cecília C.C. Silva, Camila M. Maroneze and Maiuí N. L.

Camargo

Institute of Chemistry - Unicamp Cidade Universitária Zeferino Vaz, P.O.Box 6154, 13083-970, Campinas, SP, Brazil Kubota@iqm.unicamp.br

In the past ten years, carbon nanotubes (CNTs) have been incorporated in electrochemical sensors to decrease overpotential and improve sensitivity [1]. In this sense, many new strategies to apply this kind of material have appeared showing the importance of CNTs in the electroanalytical field. Several examples of strategies of the uses of carbon nanotubes in the preparation of amperometric sensors for electrocatalytical detection of biomolecules of interests like NADH and l-cysteine (Cys) will be discussed. The development of sensors based on functional platforms to metal ions complex immobilization on multi-walled carbon nanotubes (MWCNTs) modified with polymers like chitosan and poly-4-vinylpyridine (PVP) will be presented. The obtained sensors showing high selectivity for the response to the analytes at a very low applied potential, indicates the promising strategies of the use of CNTs for sensors development.

The use of graphene oxide in both reduced and oxidized forms for electrochemical purposed has been extensively reported in the literature as recently reviewed [2]. Most of the works prepare graphene oxide by chemical exfoliation of graphite employing strong and concentrated oxidant and acid, however no systematic studies are performed to show the properties and characteristics of the graphene oxide obtained by the different procedures. The different routes to prepare reduced graphene oxide (r-RGO) will be demonstrated and showing that the most adequate procedure to prepare it for electroanalytical purpose is by simply applying the potential of +1.8 V vs. SCE on the glassy carbon electrode. This procedure generates similar electrochemical properties as graphene oxide allowing controlling the degree of reduction. The similarity of oxidized GCE and graphene oxide was characterized by Cyclic voltammetry, EIS, Raman and XPS analysis. Our results clearly indicate that the electrochemical response of graphene oxide resides in the oxygen functional groups.

Furthermore, carbon nanomaterials (CNTs and graphene) have been the center of attention for the development of advanced electronic devices, mainly the field effect transistors (FETs) [3]. Because their electrical conductivity can be modified through interaction with chemical or biological species and as their dimensions are comparable to the analyte to be detected, these carbon nanomaterials based devices present a high electrical sensitivity. We will present the independent and separated wafer-scale assembly of a high density of single-walled carbon nanotubes (SWCNTs) and graphene as gate of the FETs. In the following step, we explored their application in the development of arrays of devices based on FETs aiming to apply these devices as (bio)sensors to detect proteins and cancer biomarkers.

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# Electrically Controlled Drug Delivery from a Reduced Graphene Oxide Composite Hydrogel

Nicky Mac Kenna,<sup>a</sup> Paul Calvert,<sup>b</sup> Aoife Morrin,<sup>a</sup> Gordon G. Wallace<sup>c</sup> and Simon E. Moulton<sup>c</sup> <sup>a</sup> National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland. <sup>b</sup> Bioengineering, University of Massachusetts Dartmouth, Dartmouth, USA. <sup>c</sup> ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2522, Australia. E-mail: nicky.mackenna2@mail.dcu.ie

Intelligent drug carriers capable of controlled drug delivery are highly desirable. In comparison with traditional routes of drug administration (i.e. oral and injection methods), on-demand drug delivery offers safer, more effective medical treatment by enabling site-specific administration with on-off regulation in real time.

In this work, reduced graphene oxide (rGO) has been composited with a Jeffamine-based hydrogel to fabricate a novel electro-conductive hydrogel system. A high loading of rGO (20% w/w) was incorporated into the hydrogel in a single polymerisation step. The swelling response, morphology, mechanical and electrochemical properties of the composite hydrogel were investigated. Enhanced electrical and mechanical properties were observed with increased rGO content.

Passive and electro-stimulated release of methyl orange (MO) from these gels was explored. MO was utilized as a model anionic drug and was expelled/retained from the composite hydrogel according to the applied electrical stimulus. A significant reduction in passive release of the dye was observed by incorporating rGO. In addition, the high surface area of rGO permitted use of low applied potentials for electro-stimulation. The release rate and dosage were tuned through variation of the % w/w rGO, as well as the polarity and amplitude of the applied electric potential. A wide number of drug release profiles were observed, ranging from slow release of low dosages to rapid release of high dosages. A high level of control and flexibility was achieved demonstrating the great potential of this delivery platform for localised drug delivery applications<sup>1</sup>.

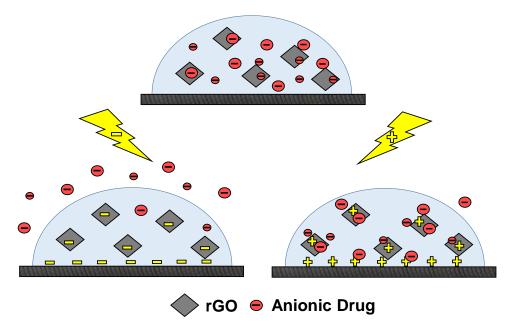


Figure 1. Schematic of electro-stimulated drug delivery from a rGO composite hydrogel. Adapted from [1].

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# The reproducibility of properties of PAN-based graphite fibres after thermal treatment

## <u>Thomas J. Rabbow</u>, Markus Trampert, Peter Pokorny, Paul Binder, Adam Whitehead *Cellstrom GmbH Industriezentrum NÖ Süd Straße 3, Objekt M36 AT-2355 Wiener Neudorf, Austria thomas.rabbow@gildemeister.com*

Carbon felts are well suited as electrochemical electrode materials due to high overvoltages for hydrogen and oxygen evolution reaction, which leads to a broad electrochemical window. In addition, the high surface area of felts makes them advantageous for transport-limited reactions. Unfortunately pure graphite has a poor wettability and pre-treatments are necessary for most applications. Especially for redox flow batteries, a high wettability is needed to ensure low flow resistance through the felt electrodes inside a stack.

As a commercial manufacturer of vanadium redox flow batteries we are dealing with large amounts of felts (many thousand square meters per year) and have to ensure the quality after activation. In contrast to many previous studies on graphite felts our focus lies in the reproducibility of the activation between different batches of felt. The aim of this work is to understand the fundamental differences between and minimize the practical variances of commercial graphitic felt after pretreatment. For example, significant variability is observed in the mass loss and wettability, despite the felts coming from one supplier. The bulk quality can be regarded as the same, as demonstrated by XRD and Rietveld analysis. However, the surface properties play a critical role during thermal reactions at moderate temperatures, as well as for electrochemical experiments.

By the Boehm method acidic and basic oxides are estimated. It generally accepted in the literature that a good wettability of carbon and graphite is achieved if the surfaces possess predominantly acidic oxides and that the basic oxides decrease the wettability. The quantity of basic and acidic surface groups are decreased with increasing temperature of activation. However, no clear evidence is found in this work for a predominance of acidic over basic groups, for those felts which exhibit a good wettability. Moreover it could be shown that the activation leads to a formation of neutral quinone groups, which are quantified by cyclic voltammetry. The results show that a good wetting is connected to establishing a minimum coverage of quinones. As soon as the felts contain quinones above a certain threshold after the activation a good wettability is established.

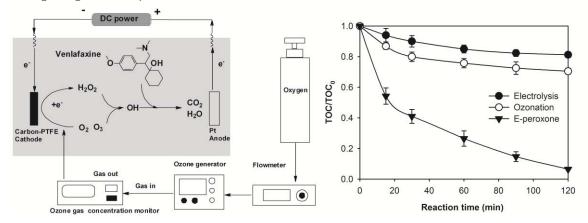
# Degradation of the antidepressant venlafaxine by electro-peroxone process

Xiang Li, Yujue Wang, Gang Yu

School of Environment, State Key Joint Laboratory of Environmental Simulation and Pollution Control, THU–VEOLIA Joint Research Center for Advanced Environmental Technology, Tsinghua University, Beijing 100084, China

e-mail address: l-xiang11@mails.tsinghua.edu.cn

This work aimed to investigate the degradation of the antidepressant drug venlafaxine (VEN) by the electro-peroxone (E-peroxone) process. The E-peroxone process combines conventional ozonation with electrolysis process, and uses a carbon-polytetrafluoroethylene cathode to electrochemically generate  $H_2O_2$  from  $O_2$  in the sparged ozone generator effluent ( $O_2$  and  $O_3$  mixture) (Yuan et al. 2013). The in-situ generated  $H_2O_2$  then reacts with the sparged  $O_3$  to produce •OH, which is a much stronger oxidant than  $O_3$  and can non-selectively oxidize most organics very rapidly. Results show that the E-peroxone process mineralized VEN and its intermediates much more rapidly than ozonation and electrolysis (Fig. 1). Effects of key operation parameters (e.g., current,  $O_3$  concentration, and solution pH) on TOC elimination were evaluated systematically. Finally, a plausible degradation pathway of VEN during the E-peroxone process was proposed based on intermediates identified by LC/ESI-TOF-MS. The results of this study indicate that the E-peroxone process can provide an effective and environmentally-friendly technology for degrading VEN in aqueous medium.



**Fig. 1.** Comparison of Venlafaxine mineralization in the ozonation, electrolysis, and E-peroxone treatment (initial concentration of venlafaxine = 20 mg/L; volume = 300 ml; initial pH = 7.9 (uncontrolled); inlet  $O_3$  gas phase concentration = 40 mg/L; sparging gas flow rate = 250 L/min; current = 300 mA. Error bars represent the standard deviation of triplicate experiments).

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# The Electrochemical Properties of Diamond and Tetrahedral Amorphous Carbon Electrodes in Room Temperature Ionic Liquids

<u>Greg M. Swain</u>, Romana Jarosova, Catherine Munson Department of Chemistry Michigan State University East Lansing, MI 48824-1322 USA swain@chemistry.msu.edu

Room temperature ionic liquids (RTILs) are emerging as a new medium for redox reactions as these liquids possess high solubilizing power, electrical conductivity, wide breakdown voltage and low volatility. Being composed entirely of ions (no solvent) and possessing wide electrochemical windows (*ca.* 5 V), it is not difficult to see why these liquids are viewed by electrochemists to be attractive electrolytes for investigation. Our group is (i) studying the wetting of these ionic fluids on different carbon electrode surfaces and how this wetting affects the capacitance-potential relationships and (ii) investigating how the carbon electrode surface chemistry and microstructure affect the heterogeneous electron-transfer rate constant of different inorganic and organic redox systems in these ionic liquids. It is well established that the in aqueous electrolyte solutions, the heterogeneous electron-transfer rate constant for certain redox-systems at ordered HOPG and more microstructurally-disordered glassy carbon is strongly affected by the electrode surface microstructure and chemistry. We seek to learn if these same trends hold in ionic liquids.

In this presentation, we will compare the electrochemical behavior of boron-doped nanocrystalline diamond and nitrogen-incorporated tetrahedral amorphous carbon thinfilm electrodes. Specifically, contact angle measurements of the surface wettability, measurements of the double-layer capacitance ( $C_{dl}$ ) and its variation with potential, and heterogeneous electron-transfer rate constants for redox systems in structurally distinct RTILs will be presented. These two carbon electrodes have distinct microstructures as compared to their sp<sup>2</sup> carbon counterparts. Nitrogen-incorporated tetrahedral amorphous carbon (ta-C:N) is a composite material consisting of a mixture of sp<sup>2</sup> and sp<sup>3</sup>-bonded carbon. Impurities can be incorporated during growth (*e.g.*, N) further adding to their complex structure. These films typically possess 40-60% sp<sup>3</sup>-bonded carbon. It has been widely used as a protective coating due to its hardness, high wear resistance and low coefficient of friction. The growth temperature for ta-C is usually from 25 to about 100 °C. This means that non-traditional materials, such as plastics, can be used as substrates for deposition. Importantly, these carbon materials possess some electrochemical properties that are similar to those of diamond.

# Potentialities of a boron doped diamond substrate for a two-step electrochemical process including sample mineralization and lead(II) assay in synthetic and real media

L. Pujol<sup>1,2,3</sup>, D. Evrard<sup>1,2</sup>, P. Gros<sup>1,2</sup>, M. Freyssinier<sup>3</sup>, A. Ruffien Ciszak<sup>3</sup>, K. Groenen Serrano<sup>1,2,\*</sup>

<sup>1</sup> Université de Toulouse, UPS, INPT, Laboratoire de Génie Chimique, 118 Route de Narbonne, F-31062 Toulouse, France <sup>2</sup> CNRS, Laboratoire de Génie Chimique, F-31062 Toulouse, France

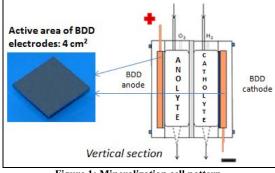
<sup>3</sup> ELTA, 14 place Marcel Dassault 31702 Blagnac, France

Because of their wide overspread in natural media, heavy metals represent a growing environmental <sup>[1]</sup> and public health <sup>[2]</sup> concern. In 2000, the European Water Frame Directive pointed them out as priority substances and established their maximal acceptable and annual average concentrations values in surface waters <sup>[3]</sup>. As a consequence, the monitoring of heavy metals is of critical importance for both environmental assessments and public health preservation.

Electrochemical devices are particularly well-suited to fulfil these needs because of the manifold advantages they exhibits over other techniques such as spectroscopies: they are usually cheap, user-friendly, and require few energy and simple procedures. They may also be reagentless and suitable for miniaturization and automated *in situ* measurements allowing on-line monitoring in real time with minimal sample contamination. Nevertheless specific developments are still required to improve sensitivity, limit of detection (LOD) and automation.

In this context, a two-step electrochemical process including a mineralization cell (Fig. 1) and an analytical chamber for lead(II) traces detection has been developed. The first one allows degradation of organic matter - which can complex free or labile Pb(II) - by means of hydroxyl radicals production on boron-doped diamond (BDD) anode. Using galvanostatic electrolysis the mineralization efficiency was remarkable with organic matter degradation about 95 % in 600 s.

The second step concerns Pb(II) assay in the analytical chamber on a BDD cathode where lead reduction was selective since water reduction was shifted to more negative potentials. Linear voltammetry, linear sweep anodic stripping voltammetry and differential pulse anodic stripping voltammetry (DPASV) were successively used with decreasing lead concentration ranges. In the latter case linear calibration curves were obtained for concentrations between 50 ppb and 10 ppm with a deposition time of 5 s (1ppm < [Pb(II)] < 10ppm) or 600s (50 ppb < [Pb(II)] < 1.2 ppm) (Fig. 2) and a potential deposition E=-1.2V/Ag/AgCI. The total analysis time was between 10 and 20 min.



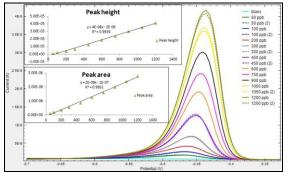


Figure 1: Mineralization cell pattern.

Figure 2: DPASVs of increasing Pb<sup>2+</sup> concentrations from 50 to 1200 ppb recorded on a BDD electrode. Deposition at -1.2 V vs Ag/AgCl/Cl<sup>-</sup> (sat.) for 600 s in 0.01 M HNO<sub>3</sub>.

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## CARBON PASTE BASED BIOSENSORS FOR ANTIOXIDANT CAPACITY

Eric de Souza Gil\*; Stephen Rathinaraj Benjamin; Jhéssica Cavalcante de Souza Golveia; Luane Ferreira Garcia; Mariângela Fontes Santiago; Flávio Marques Lopes.

\*Department a Faculty of Pharmacy, Federal University of Goias, Av. Universitária s/n, 74605-220 Goiânia, GO, Brazil.

### E-mail: ericsgil@gmail.com

### Abstract:

Recently, it was shown that the antioxidants have large and essential influence on human health. In fact, the protective effects of food products against cardiovascular diseases, cancer and ageing. have been attributed to polyphenol content. In turn, the polyphenolic compounds which are recognized by their remarkable antioxidant activity can be easily estimated by polyphenol oxidases based biosensors. Thus, taking into account the relevance of such determination in order to evaluate the nutraceutical quality of beverages, fruits and other foodstuffs, many biosensors have been proposed. Among them, the carbon paste devices are highlighted by the easy preparation and surface renewal (Rodrigues and Rivas, 2002).

This work describes the development of carbon paste amperometric biosensors, based on laccase for evaluation of antioxidant activity expressed by means of total polyphenol content. The biosensors were constructed by occlusion of laccase (*Pycnoporus sanguineus*) crude extract (2019 U.L<sup>-1</sup>) in different carbon paste based composites. The electrochemical properties of the resulting composites, namely Carbon Paste-Laccase (CPL) modified with Bovine Serum Albumin (CPL-BSA), Chitosan (CPL- C), Silica (CPL-S), Titanium dioxide (CPL-T), DNA (CPL-D), Carbon Nanotubes (CPL-CN), non-activated Carbon Nanotubes plus DNA (CPL-DnCN) and activated Carbon Nanotubes plus DNA (CPL-DCN) were evaluated by voltammetry in different experimental conditions.

The added amount of each modifier to the carbon paste was based on previous knowledge and on literature data (Popescu, 1995; Rodrigues and Rivas, 2002). Nevertheless, the main aim of this work was to check the effect of each type of modifier on the improvement of CPL performance in order to express the antioxidant activity and total polyphenol content of complex natural samples such as coffee beverages. In order, the effect of electrolyte composition, pH, scan rate, pulse amplitude, response time and concentration range were carefully evaluated, whereas rutin and/or caffeic acid were employed as standard solutions.

The higher sensitivity,  $0.0549\mu A/\mu M$ , and lower detection limit, 1,2  $\mu M$ , was obtained for CPL-DCN. The determination of rutin was achieved in the linear range from 20 to 140  $\mu M$  (r = 0.9987). In addition, the biosensor demonstrated suitable stability over 10 days and good repeatability (RSD < 5%).

CPL-DCN was used for the determination of total phenol content of coffee samples, expressed as Rutin Equivalents (REq) and the results were compared with those from the DPPH and Folin–Ciocalteu spectrophotometric methods (Lino et al, 2013). Further the inherent sensitivity of electroanalytical methods, the amperometric biosensor exhibits some interesting advantages such as simplicity due to the minimal sample preparation and leading to rapidity of antioxidant capacity assay.

Keywords: laccase; Pycnoporus sanguineus; carbon paste electrode; DPV; antioxidant capacity.

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# Application of Electrochemically and Chemically Reduced Graphene Oxide Noncovalently Modified with Tetrathiafulvalene for Glucose Biosensing

Barbara Kowalewska, Adrian Patyna Department of Chemistry, University of Warsaw Pasteura 1, PL-02-093 Warsaw, Poland bstar@chem.uw.edu.pl

Graphene, a two-dimensional nanomaterial, constitutes a new carbon comprising layers of carbon atoms arranged in six-membered rings [1]. It has attracted intense attention due to its unique electronic, thermal and mechanical properties. Graphene possesses a high ratio of surface area, a good conductivity and mechanical properties comparable with (or even better) than carbon nanotubes. Owing to its inert chemical property and highly hydrophobic surface, graphene is considered as an ideal support for redox mediators via  $\pi$ - $\pi$  stacking interactions [2].

Many chemical methods have been developed for the preparation of graphene, such as epitaxial growth on silicon carbide and chemical reduction of graphene oxide (GO). As the oxidized form of graphene, GO could be easily obtained via a simple chemical processing of graphite. GO contains a range of reactive oxygen containing functional groups, which endows it water solubility and possibility for further biological applications. However, excess of oxygen may break the sp<sup>2</sup> structure of graphene, as a result deteriorate its conductivity.

In the present work, we have exploited unique characteristics of reduced graphene oxide (GO) (obtained by electrochemical treatments (ERGO) and chemical treatments with hydrazine (CRGO)) to construct the efficient anodic glucose oxidase based bioelectrocatalytic systems of potential utility for biofuel cells and biosensors. A noncovalent modification method of ERGO and CRGO conducting support with a mediator, tetrathiafulvalene (TTF), and the bioelectrocatalytic activities of ERGO-TTF and CRGO-TTF composites with immobilized glucose oxidase toward the oxidation of glucose have been demonstrated.

The presence of TTF is expected to facilitate an effective flow of electrons from the redox centers of glucose oxidase to the glassy carbon electrode [3]. TTF and its derivatives constitute a group of redox molecules that were successfully used as redox mediators in enzyme electrochemistry. Due to the existence of hydrophilic cation-exchange domains within Nafion deposits on graphene, capable of retaining soluble TTF<sup>+</sup>, the overall stability of the our bioelectrocatalytic film has increased. As before, reduced graphene oxide have supported transport of electrons within the bio-electrocatalytic system. On the whole, combination of TTF-graphene and glucose oxidase within the film (deposited onto glassy carbon electrode substrate) has produced a catalytic system capable of effective oxidation of glucose in 0.1 M phosphate buffer (pH=8.0). The formation, morphology, and electrocatalytic reactivity of our bioelectrocatalytic films containing of TTF-modified graphene were examined using cyclic voltammetry, rotating disk voltammetry, FTIR spectroscopy, transmission and scanning electrochemical microscopy.

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# N-doped graphitic carbons as electrocatalysts for the synthesis of hydroxylamine with cogeneration of electricity.

<sup>a</sup> <u>Nick Daems</u><sup>a</sup>, Patrick Steegstra<sup>b</sup>, Annick Hubin<sup>b</sup>, Ivo F.J. Vankelecom<sup>a</sup> and Paolo P. Pescarmona<sup>a,c</sup> <sup>a</sup> Centre for Surface Chemistry and Catalysis, K.U. Leuven, Kasteelpark Arenberg 23, post box 2461, 3001 Heverlee, Belgium.

<sup>b</sup> Vrije Universiteit Brussel, Research Group Electrochemical and Surface Engineering, Pleinlaan 2, 1050 Brussel, Belgium.

<sup>c</sup> Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

nick.daems@biw.kuleuven.be

The cogeneration of electricity and valuable chemicals in a fuel cell is an emerging field of research in the context of sustainability [1]. An interesting example thereof is the cogeneration of electricity and hydroxylamine (NH<sub>2</sub>OH) in a H<sub>2</sub>/NO fuel cell [2]. This process allows the conversion of NO, a common waste product in car exhaust gases, into hydroxylamine, which is widely used in industry for the synthesis of cyclohexanone oximine, an intermediate in the production of nylon 6. The development of a suitable electrocatalyst is of crucial importance for achieving high currents and selectivities towards hydroxylamine in a H2/NO fuel cell.

Here, we present novel electrocatalysts for the conversion of NO to hydroxylamine, based on N-doped graphitic carbon materials prepared by controlled pyrolysis of polyaniline containing non-noble metal centers [3]. These materials display important assets: (1) isolated metal centers, which promote the selectively towards hydroxylamine over side-products containing two N atoms (e.g. N2O and N2); (2) metals with at least two accessible oxidation states to successfully adsorb NO and initiate its reduction; (3) an extended delocalized  $\pi$ -system of the N-doped carbon granting good conductivity.

The polyaniline-based electrocatalysts were synthesized by varying the metal species (Mn, Fe, Al, Cu and Cu) and loading, the pyrolysis temperature and duration and by studying the effect of the extent of acid leaching to remove inactive metal species. The performance of these electrocatalysts in the reduction of NO was evaluated by means of linear sweep voltammetry (LSV) with a 100% NO gas feed in a high-throughput setup containing four cathode half cells. The nature of the metal center proved to strongly affect the electrocatalyst performance in terms of onset potential and current densities. A thorough removal of inactive metal sulfates by acid leaching was found to be crucial to enhance the activity of the electrocatalysts (Fig. 1A). Further investigations showed that the presence of metal species in the electrocatalyst is not strictly required for the NO reduction: an N-doped ordered mesoporous graphitic carbon material (NOMC) synthesized through a novel templating method showed competitive performance compared to the polyaniline-based electrocatalyst with iron centers (Fig. 1B). The results highlight the potential of N-doped graphitic carbon electrocatalysts for the reduction of NO to hydroxylamine.

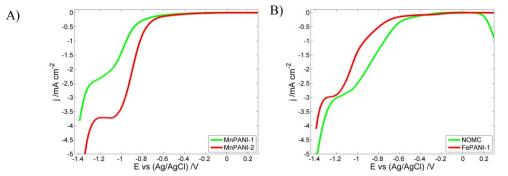


Figure 1: (A) LSV plots of manganese-containing electrocatalysts without and with extra leaching step, MnPANI-1 and MnPANI-2, respectively and (B) LSV plots of the iron-containing electrocatalyst (FePANI-1) and N-doped ordered mesoporous graphitic carbon electrocatalys (NOMC).

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# Electrochemical Study of Dopamine at Metal Oxide doped Phthalocyanine supported on Carbon Nanotubes Modified Glassy Carbon Electrode Platform

Ntsoaki Mphuthi<sup>\*1,2</sup>, Abolanle S. Adekunle<sup>1,2,3</sup>, Eno. E. Ebenso<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, School of Mathematics and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus) Private Bag X2046, Mmabatho 2735, South Africa.
<sup>2</sup>Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus) Private Bag X2046, Mmabatho 2735, South Africa.
<sup>3</sup>Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife, Nigeria. mphuthi.ntsoaki@gmail.com, Eno.Ebenso@nwu.ac.za

Dopamine (DA) is a neurotransmitter in mammalian brain tissues that belongs to the family of inhibitory neurotransmitters. It plays an important physiological role in the functioning of central nervous, renal, hormonal and cardiovascular systems as an extra cellular chemical messenger. Abnormal DA level may relate to many diseases, such as Parkinson's disease, Huntington's disease and Alzheimer's diseases, where the dopaminergic activity is lower than in healthy individuals. The opposite is true in schizophrenia where the activity of the dopaminergic neurons is increased due to abnormalities in their regulation. It is also known that with a bare electrode the oxidation peaks of DA at nearly same potential with that of ascorbic acid (AA) and uric acid (UA), which results in the overlapped voltammetric responses making their discrimination very difficult. Thus, motivation to this work is to fabricate sensitive, specific and selective electrochemical sensors that would discriminately detect DA in the presence of other interfering species such as AA and UA. Electrochemical sensing has been proven as simple analytical method that can determine the presence of a wide range of substances at relevant concentration levels with sufficient selectivity, sensitivity, reproducibility, and they are small, inexpensive, relatively simple to fabricate, easily implantable, and can provide real-time measurements. Other analytical techniques such as chromatographic methods, mass spectroscopy, spectrophotometry, fluorometry etc., are reported to be relatively expensive and require long time analysis.

In this study, the electron transfer and catalytic properties of glassy carbon electrode (GCE) modified with Phthalocyanine (Pc) doped with zinc oxide (ZnO) and iron (II, III) oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles respectively, supported on multi-walled carbon nanotubes (MWCNT) was investigated. Successful synthesis of the nanomaterial's was confirmed using spectroscopic and microscopic techniques such as FTIR, UV-vis, Raman, XRD, EDX, SEM and TEM, while successful modification of the electrode was confirmed using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The developed sensors include GCE-MWCNT, GCE-Pc-Fe<sub>3</sub>O<sub>4</sub>, GCE-ZnO, GCE-MWCNT-ZnO, GCE-MWCNT-Pc-ZnO, GCE-MWCNT-Fe<sub>3</sub>O<sub>4</sub> and GCE-MWCNT-Pc-Fe<sub>3</sub>O<sub>4</sub>. Electron transfer properties of the modified GCE was investigated in 0.1 M PBS (pH 7.0) and 5 mM Ferri/Ferro ([Fe(CN)<sub>6</sub>]<sup>3-/4</sup>) redox probe using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The modified electrodes were applied for the determination of DA in 0.1 M PBS (pH 7.0) using CV and EIS with satisfactory results. The interfering effect of AA on DA determination was investigated, and the DA detection and quantification in real life sample was carried out and will be discussed.

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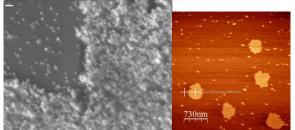
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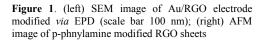
## **Electrochemistry of Graphene Deposited by Different Methods**

Lucas Lodovico<sup>1</sup>, Elaine Yoshiko Matsubara<sup>2</sup>, José Maurício Rosolen<sup>2</sup>, <u>Roberto M. Torresi<sup>1</sup></u> <sup>1</sup>Instituto de Química - Universidade de São Paulo - Postal code: 26077 - 05513-970 São Paulo - Brazil - rtorresi@iq.usp.br

<sup>2</sup>Depto de Química, FFCLRP, Universidade de São Paulo, Ribeirão Preto, SP, Brazil

Graphene is a novel material with potential application in electrochemistry<sup>1,2</sup> due to, especially, its outstanding electrical conductivity and specific area, around 2600 m<sup>2</sup> g<sup>-1</sup>. In energy storage, these properties make graphene a candidate for use as electrode material in electrochemical capacitors, or as conductivity enhancer in batteries. Both of these applications rely on the maximum utilization of the active area of the material. As such, a proper design of the electrode is necessary, since, for instance, restacking of graphene sheets can negatively impact the specific capacitance of an electrochemical capacitor<sup>3</sup>. Most works on the literature, however, pay little attention to the morphology of the graphene sheets on the final electrode construction, such that maximum utilization of graphene's area might not be taking place. In this work, two novel approaches have been taken to ensure a controlled electrode morphology.





The first approach is based on the electrophoretic deposition (EPD) of graphene oxide sheets over an electrode, followed by its reduction. As seen in figure 1, this leads to an extremely rough deposit, with a high surface area. This was found out to be due to the intrinsic deposition kinetics of electrophoresis. During EPD, sheets with higher charge to weigh ratio, i.e., the smaller ones, will have a higher mobility, and preferentially adhere to the surface. This showed to be very beneficial to use in an electrochemical capacitor, with a great value of capacitance observed.

Another approach studied is the use of diazonium electrochemistry to attach graphene sheets to the electrode. In this approach, reduced graphene oxide (RGO) was modified with p-phenylamine groups over its basal plane, which leads to the sheets seen in figure 1. These sheets possess amine groups that can be further converted into diazonium cations. Diazonium is easily reduced electrochemically to form a covalent bond between the electrode's surface and the sheet. Deposits thusly obtained were shown to be only one sheet thick and to be strongly adhered to the surface. The deposited layer can also be easily grown beyond one sheet, by continuing the electrochemical deposition of modified RGO *via* diazonium electrochemistry.

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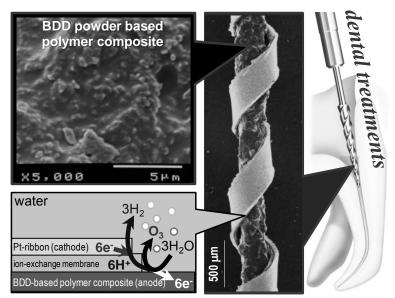
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# Flexible Pinpoint Electrolysis Unit Coated with Boron-doped Diamond Powder (BDDP) Based Polymer Composites for Dental Treatments

<u>Tsuyoshi Ochiai</u>,<sup>1,2</sup> Mio Hayashi,<sup>1</sup> Shoko Tago,<sup>1</sup> Kazuo Hirota,<sup>3</sup> Takeshi Kondo,<sup>2</sup> Kazuhito Satomura,<sup>4</sup> Akira Fujishima<sup>1,2</sup>

<sup>1</sup>Photocatalyst Group, Kanagawa Academy of Science and Technology, KSP East 407, 3-2-1 Sakado, Takatsu-ku, Kawasaki City, Kanagawa 213-0012, Japan, <sup>2</sup>Photocatalysis International Research Center, Tokyo University of Science, Japan, <sup>3</sup>Research & Development Department, GC Corporation, 76-1 Hasunuma-cho, Itabashi-ku, Tokyo 174-8585, Japan, <sup>4</sup>Department of Oral Medicine, School of Dental Medicine, Tsurumi University, 2-1-3 Tsurumi, Tsurumi-ku, Yokohama 230-8501, Japan pg-ochiai@newkast.or.jp

You might have experienced... when the cavity has reached the pulp, we have to remove dead and infected material away from a root canal of the teeth with dental instruments, and then sterilize the root canal by NaClO. This is conventional "root-canal therapy". However, sometime remaining bacteria can lead to not only periapiral periodontitis but also serious health issues. Recently, we have reported a pinpoint electrolysis unit with BDD microelectrode and its great potential for dental treatments such as sterilization of root-canal [1]. However, inflexible polycrystalline BDD film peeled off from the substrates easily. In this study, we devise flexible pinpoint



**Figure 1.** Schematic image of the flexible pinpoint electrolysis unit with BDDP-based polymer composites.

electrolysis unit by using of BDDP-based polymer composite for dental treatment (Figure 1).

The unit was prepared as follows. The dental instruments' surface were coated by BDDP-based polymer composite consist of BDDP [2] and 20% Nafion<sup>®</sup> Dispersion Solution DE2021 at a specified mixing ratio as an anode. A Pt-ribbon coated with Nafion<sup>®</sup> Dispersion Solution was spirally wound around the dental instruments' surface as a cathode. When DC voltage was applied between the anode and the cathode in the water, ozone and oxidative intermediates can be generated. The unit showed almost the same sterilization ability as 1 wt% of aqueous NaClO treatment in *in vitro* assessment in the root-canal of bovine teeth. Moreover, the BDDP-based polymer composite has excellent durability which hardly causes cracks and peeling off even by repeated bending while the electrolysis. The superiority of BDDP-based polymer composite over simple and easy-to-handle pinpoint electrolysis unit, in terms of the flexibility, durability, and disinfection activity was demonstrated with the conventional methods and conditions. This research is attractive to develop a practical unit for dental treatment.

### Acknowledgements

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# A Sensor for Determination of Serotonin in Human Urine using a Multi-Walled Carbon Nanotube/Ni, Zn and Fe Oxides Composites Modified Glassy Carbon Electrode

Omolola E. Fayemi<sup>\*1,2</sup>, Abolanle S. Adekunle<sup>1,2,3</sup>, Eno. E. Ebenso<sup>1,2</sup>

<sup>1</sup>Department of Chemistry, School of Mathematics and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus) Private Bag X2046, Mmabatho 2735, South Africa.

<sup>2</sup>Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus) Private Bag X2046, Mmabatho 2735, South Africa.

<sup>3</sup>Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife, Nigeria. <u>fomololaesther@yahoo.com</u>, Eno.Ebenso@nwu.ac.za

There is significant interest in developing electrochemical techniques for determination of neurotransmitters such as serotonin (5-HT). 5-Hydroxytryptamine (serotonin, 5-HT) is an important and major biogenic monoamine neurotransmitter as well as neuromodulator [1], widely distributed in human brain and makes an important contribution in wide variety of biological, physical, psychopathological processes including sleep regulation, depression, eating disorder, alcoholism, infantile autism, anxiety disorders, muscle contraction, liver regeneration, endocrine regulation, obsessive – compulsive disorder and psychosis [2 - 4]. The concentration of 5-HT is very low in biological systems and the other problem which must be solved in the electrochemical detection of 5-HT is the co-existence of many interfering compounds in biological systems. Among these interfering compounds, ascorbic acid (AA), and dopamine (DA) are particularly important because they can all be oxidized at similar potentials resulting in overlap of voltammetric responses. The oxidation potential of 5-HT (pH 7, 0.38 V) is close to that of DA (0.22 V) and AA (0.2 V) on the unmodified glassy carbon electrodes. To overcome these problems, one of the most common ways is using a modified electrode to improve the measuring sensitivity of 5-HT and remove the interference of AA and DA to 5-HT detection. Therefore, different electrochemical methods using various modified electrodes were proposed for the determination of 5-HT.

In this work, a fast and sensitive voltammetric method has been proposed for the determination of serotonin in human urine using multi-walled-carbon-nanotube-doped with nickel, zinc and iron oxide modified glassy carbon electrode (GCE-MWCNT-MO). Field emission scanning electron microscopy (FE-SEM), FTIR, XRD, UV–vis spectroscopy, Raman spectroscopy, XRD, EDX, cyclic voltammetry techniques and electrochemical impedance (EIS) were used for the characterization of the modified sensors. The electrochemical response of serotonin was determined by square wave voltammetry (SWV) in phosphate buffer solution (PBS) at physiological pH 7. The electrochemical measurements were carried out using square wave voltammetry and cyclic voltammetry. The modified GCE-MWCNT-MO exhibit excellent electrocatalytic activity towards the electrochemical oxidation of serotonin exhibiting a large peak current and shift of peak potential to less positive potentials as compared to unmodified electrode. The concentration range for the serotonin determination was between 4 x 10<sup>-5</sup>  $\mu$ M to 6.25  $\mu$ M with detection limits of 0.1, 9.88 and 7.68  $\mu$ M for GCE-MWCNT-ZnO, GCE-MWCNT-NiO and GCE-MWCNT-Fe<sub>3</sub>O<sub>4</sub> respectively. The common metabolites such as ascorbic acid and dopamine do not interfere over this range of concentrations which show the selectivity of the developed sensors. The determination of serotonin in human urine was carried out and will be discussed.

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## Implementation of Metallic Clathrochelates at the Surface of **Carbonaceous Substrates for Hydrogen Evolution in Acidic Media**

Pierre Millet, A. Ragupathy, A. Villagra, A. Ranjbari Université Paris-Sud, ICMMO, bât. 410, 91405 Orsay cedex France pierre.millet@u-psud.fr

Conventional Polymer Electrolyte Membrane (PEM) water electrolyzers are using carbon-supported platinum nanoparticles at the cathode for the hydrogen evolution reaction (HER) [1]. Platinum scarcity, cost and sensitivity to surface contamination by under potential deposition of trace amounts of metallic species are all calling for alternative electrocatalysts. Whereas in alkaline water electrolysis technology, nickel and cobalt bulk particles are commonly used as electrocatalysts, their direct implementation at the cathode of PEM water electrolyzers is not a straightforward task because of the strong acidity of the polymer electrolyte (equivalent to that of molar sulfuric acid solutions) that tends to corrode (dissolve) particles at open circuit conditions. Over the last years, our approach was to use molecular chemistry to bypass the problem [2,3]. Metallic molecular complexes such as the clathrochelates pictured in figure 1 offer several advantages compared to nanoparticles: (i) non noble metals can be used as active centers; (ii) only limited amounts of metals are required; (iii) redox properties of active centers can be tuned to desirable values by selecting appropriate organic ligands; (iv) ligands can be used as chemical linkers for efficient surface functionalization. The purpose of this communication is to discuss different issues related to the implementation of cobalt clathrochelates at the surface of model (graphene, glassy carbon) and real (carbon powder and fibers) carbonaceaous substrates in view of practical application in PEM water electrolyzers. In particular, the conditions that are required for the adsorption of monolayer thick molecular coatings are discussed. Electrochemical features (figure 2), performance and durability characteristics with regard to the HER are also presented.

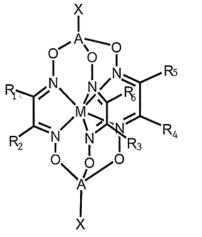


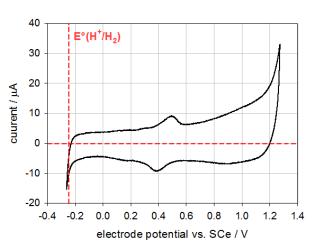
Fig. 1: general structure of metal clathrochelates. M = Co, Ni, Fe. R = alkyls,aryls. X = halogen, alkyl.

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Fig. 2: cyclic voltamogram measured on glassy carbon, surface coated by adsorption of a cobalt clathrochelate (R = H, X = n-butane).  $H_2SO_4 0.5M$ ; 10 mV/s, 25°C.



# Hydroxyl Radicals Electrochemically Generated In Situ at a Boron Doped Diamond Electrode Surface: Interaction with Biological Compounds

### <u>Ana Maria Oliveira-Brett</u>\*, T. Adrian Enache, S. Carlos B. Oliveira Department of Chemistry, Faculty of Science and Technology, University of Coimbra, 3004-535 Coimbra, Portugal \*brett@ci.uc.pt

The interaction of hydroxyl radicals electrochemically generated *in situ* at a boron-doped diamond electrode (BDDE) with amino acids, peptides, proteins and DNA has been investigated. The BDDE has weak adsorption properties, an excellent positive potential window, and at high positive potentials the *in situ* electrochemical generation, by water discharge, of hydroxyl radicals (OH<sup>•</sup>) occurs. The oxidation of biological compounds at the BDDE surface follows one of two different mechanisms depending on the applied potential. In the region of water stability, before oxygen evolution, only reactions involving simple electron transfer occur. At high positive applied potentials, in the potential region of oxygen evolution and water discharge, the reactivity of the biological compounds is related with their interaction with the *in situ* OH<sup>•</sup> electrogenerated at the BDDE surface, and a sequence of reactions is initiated. The BDDE is relatively unreactive, but not completely inert, and the electrogenerated hydroxyl radicals play a role as mediator in the oxidation of biological compounds.

The electrochemical oxidation behaviour of the electroactive amino acids at BDDE and glassy carbon electrodes (GCE) was investigated and compared. The oxidation reactions of the sulphur-containing amino acids cysteine and methionine are irreversible, diffusion-controlled pH dependent processes, and occur in a complex cascade mechanism. Cysteine undergoes three consecutive oxidation reactions at both types of electrode. Methionine undergoes a one-step oxidation reaction at BBDE due to its negligible adsorption, and oxidation leads to the formation of methionine sulfone [1]. Histidine oxidation occurs in a single-step mechanism at both electrodes with no adsorption at the carbon surface [2]. Tryptophan is oxidised at more positive potentials than tyrosine at BDDE, while at GCE the oxidation of both occurs at the same potential. This is a very important property of BDDE with applications in proteomics research [2].

*In situ* DNA oxidative damage by electrochemically generated hydroxyl free radicals has been directly demonstrated at a BDDE. The DNA-electrochemical biosensor incorporates immobilised double-stranded DNA (dsDNA) as molecular recognition element on the electrode surface, and measures *in situ* specific binding processes with dsDNA, being a complementary tool for the study of bimolecular interaction mechanisms of compounds binding to DNA and enabling the screening and evaluation of the effect on DNA of radicals and health hazardous compounds. The hydroxyl radical is considered the main contributing reactive oxygen species (ROS) to endogenous oxidation of cellular dsDNA causing double-stranded and single-stranded breaks, free bases, and occurrence of 8-oxoguanine. The dsDNA-electrochemical biosensor was used to study the interaction between dsDNA immobilized at a BDDE surface and *in situ* electrochemically generated OH<sup>•</sup>. The relevance of the dsDNA-electrochemical biosensor in the evaluation of the dsDNA-hydroxyl radical interactions was clearly demonstrated [3].

BDDE have excellent detection limits and high sensitivity which makes them useful tools for the investigation of the oxidative damage redox mechanisms of biological compounds, such as amino acids, peptides, proteins and DNA, with *in situ* OH<sup>•</sup> electrochemically generated at a BDDE surface.

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# **Degradation of Organic Pollutants from Waters Using Electrochemical Advanced Oxidation Processes with a Boron-Doped Diamond Anode**

Enric Brillas

Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Ouímica Física, Facultat de Química, Universitat de Barcelona, Martí I Franquès 1-11, 08028 Barcelona, Spain e-mail address: brillas@ub.edu

This communication presents the application of electrochemical advanced oxidation processes (EAOPs) like electrochemical oxidation (EO), electro-Fenton (EF), UVA photoelectro-Fenton (PEF) and solar photoelectro-Fenton (SPEF) to the decontamination of organics from waters using undivided tank reactor or filter-press flow cells containing a boron-doped diamond (BDD) anode. In EO, organics are destroyed by heterogeneous hydroxyl radical BDD(•OH) formed at the anode surface from water oxidation: (1)

 $BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^-$ 

In EF, a carbonaceous cathode fed with  $O_2/air$  is employed to continuously generate  $H_2O_2$  from reaction (2) and  $Fe^{2+}$  ion is added to the solution to produce homogeneous <sup>•</sup>OH in the bulk from Fenton's reaction (3) with optimum pH near 3.

 $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ 

(2) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$ (3)

Organics are then attacked by both, BDD(<sup>•</sup>OH) formed from reaction (1) and by <sup>•</sup>OH produced in the bulk from Fenton's reaction (3). The PEF and SPEF processes involve the simultaneous irradiation of the treated solution under EF conditions by UVA light and sunlight, respectively. In these methods, the mineralization of organics is enhanced by: (i) the higher  $Fe^{2+}$  regeneration and 'OH production via Fe(OH)<sup>2+</sup> photolysis by reaction (4) and (ii) the photodecomposition of Fe(III)-carboxylate species by the global reaction (5).

$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + ^{\bullet}OH$	(4)
$\operatorname{Fe(OOCR)}^{2^+} + hv \rightarrow \operatorname{Fe}^{2^+} + \operatorname{CO}_2 + \operatorname{R}^{\bullet}$	(5)

The high oxidizing ability of EO with a BDD anode will be exemplified for the degradation of chlorophenoxy herbicides, the herbicide atrazine, the drug omeprazole and the antimicrobial sulfamethazine in 100 mL stirred tank reactors with electrodes of 3 cm<sup>2</sup> area. The influence of key parameters like pH, applied current density and substrate concentration on the mineralization rate and mineralization current efficiency will be examined. In most cases, good mineralization degrees were obtained except in the case of atrazine, which is transformed into cyanuric acid. Aromatic intermediates were detected by reversed-phase HPLC and generated carboxylic acids were identified by ion-exclusion HPLC. Final carboxylic acids were mineralized under the action of generated BDD(<sup>•</sup>OH), a fact that does not take place with heterogeneous hydroxyl radicals formed at the surface of other anodes like Pt.

The comparative EO, EF, PEF and SPEF degradations of the drugs salicylic acid and ibuprofen, as well as of the drug precursor  $\alpha$ -methylphenylglycine, has been studied in a 100 mL stirred tank reactor with electrodes of 3 cm<sup>2</sup> area. The performance was found optimal at pH 3.0 in all cases and by using 0.5-1.0mM Fe<sup>2+</sup> in the three latter methods. Almost total mineralization was always reached and the current efficiency rose when current density decreased and contaminant content increased. A pseudo-first-order reaction was found for the pollutants decay. Oxalic acid, the more largely accumulated product, was quickly removed by the fast photolysis of its Fe(III) complexes. Ion chromatography revealed that the initial N of pollutants was converted into  $NH_4^+$  ion and in smaller proportion into  $NO_3^-$  ion.

The scale-up of the SPEF method to a 2.5 L flow plant with a 20 cm<sup>2</sup> BDD/O<sub>2</sub>-diffusion cell coupled to a 600 mL flat solar photoreactor will be further described. Solutions up to 200 mg  $L^{-1}$  of TOC in 0.05-0.10 M Na<sub>2</sub>SO<sub>4</sub> with 0.5 mM Fe<sup>2+</sup> at pH 3.0 and 50 mA cm<sup>-2</sup> were usually tested to obtain an almost total mineralization of the herbicide mecoprop, o-, m- and p-cresol and the dye Acid Yellow 36. The SPEF process has also been performed in a 10 L flow plant with a cell of 90.3 cm<sup>2</sup> electrodes and coupled to a 1.57 L solar compound parabolic collectors (CPCs) photoreactor to treat the beta-blockers atenolol, metoprolol tartrate and propranolol hydrochloride. For this plant, a combined reactor equipped with a BDD/air-diffusion-Pt/carbon-felt cell gave low energy consumptions close to 250 kWh kg<sup>-1</sup> TOC for >95% mineralization.

Finally, the characteristics of the degradation of atrazine using a hybrid method involving SPEF with a BDD/BDD cell and solar TiO<sub>2</sub> photocatalysis, as well as of a winery wastewater by coupling electrocoagulation and PEF with a BDD/BDD cell, will be discussed.

## Electrochemical properties of surface terminated and hybrid carbon films and their application to electroanalysis

Osamu Niwa<sup>1</sup>\*, Dai Kato<sup>1</sup>, Tomoyuki Kamata<sup>1</sup>, Shigeru Hirono<sup>2</sup>, Eisuke Kuraya<sup>3,4</sup>, Masashi Kunitake<sup>3</sup> <sup>1</sup>National Institute of Advanced Industrial Science and Technology, Central 6, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8566, Japan <sup>2</sup>JVC Afty Corporation, <sup>3</sup>Kumamoto University,<sup>4</sup>Okinawa National College of Technology

## niwa.o@aist.go.jp

The electrochemical performance of carbon film electrodes can be widely controlled depended upon surface termination or doping of other atoms such as oxygen, nitrogen and fluorine. We have been studying nanocarbon film electrodes formed by electron cyclotron resonance (ECR) sputtering and unbalanced magnetron (UBM) sputtering methods<sup>1,2</sup>. The structure of carbon films such as  $sp^2/sp^3$  ratio can be widely controlled by these sputtering methods with maintaining extremely flat surface. The surface of the carbon films are electrochemically or plasma treated to introduce oxygen and fluorine containing groups on to the surfaces. In order to fabricate nitrogen doped film, small amount of N<sub>2</sub> gas was introduced during sputtering. In contrast, pure carbon film was treated by ammonia gas to introduce nitrogen containing groups only on the film surface. As we reported previously, electrochemically treated carbon film becomes hydrophilic by significant increase in the surface oxygen concentration<sup>3</sup>. This hydrophilic and very flat surface of the carbon film can detect the amount of each bases in the single stranded DNA and successfully demonstrated SNPs and DNA methylation analysis<sup>4,5</sup> because the adsorption of biomolecules can be significantly suppressed.

A nitrogen-doped nanocarbon (N-ECR) film electrodes with mixed sp<sup>2</sup> and sp<sup>3</sup> bonds formed using ECR sputtering method has a very smooth surface with an average roughness of 0.1 to 0.2 nm, which is almost independent of nitrogen concentration<sup>6</sup>. The oxygen and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) reduction potentials at N-ECR carbon film electrode shifted about 0.3 and 0.15 V (vs. Ag/AgCl), respectively, and the peak height of H<sub>2</sub>O<sub>2</sub> is greatly increased similar to well known carbon alloy materials<sup>7</sup>. The structure and electrochemical properties of N-ECR film electrode depended upon nitrogen concentration shows some differences compared with those of nitrogen containing carbon film (ta-C:N) deposited by pulsed laser-arc deposition (PLD)<sup>8</sup>. We recently prepared nitrogen terminated carbon (NS-UBM) film by ammonia gas treatment after depositing the film by UBM sputtering and compared its electrochemical performances with those of a nitrogen doped carbon (N-UBM) film also deposited by UBM sputtering. The concentrations of both films are almost identical, which is confirmed by XPS measurement. The oxygen reduction at NS-UBM film shifts more positive compared with N-UBM film electrode, suggesting that surface groups are very important to reduce overotential for oxygen reduction.

We previously reported electrochemically stable fluorinated nanocarbon (F-ECR) film by CF<sub>4</sub> plasma treatment that had an sp<sup>2</sup> and sp<sup>3</sup> hybrid bonds<sup>9</sup>. The contact angle of the film surface increased from 72 to 93 degree after surface fluorination. The electron transfer rates at an F-ECR film electrode are as high as those of pure ECR carbon films for Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+/3+</sup>, whereas they are much slower than those of pure carbon films for Fe<sup>2+/3+</sup> and Fe(CN) <sub>6</sub><sup>3-/4-</sup>. Recently, we also employed the F-ECR film electrode to selectively detect hydrophobic antioxidants in foods and drinks. The F-ECR film electrode shows fast electron transfer for hydrophobic  $\alpha$ -tocopherol. In contrast, electrochemical responses for hydrophilic antioxidants such as ascorbic acid were effectively suppressed at the F-ECR film electrode. These properties allowed us to achieve selective and quantitative measurements of hydrophobic antioxidants with maintaining the suppression for the responses of hydrophilic antioxidants in the analyte solution.

We also fabricate a metal alloy nanoparticles dispersed carbon film electrode which is applied as a detector of HPLC for various sugar detection.

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# Electrochemical Sensor Based on Reduced Graphene Oxide Modified with Cu(II)-*meso*-Tetrathienyl Porphyrin for Determination of Endocrine Disruptor

Fernando C. Moraes, Bruno Rossi, Maria C. Donatoni, Kleber T. Oliveira and <u>Ernesto C. Pereira</u> Departamento de Química, Universidade Federal de São Carlos São Carlos, SP, Brazil *fcmoraes@hotmail.com* 

Reduced graphene oxide (RGO) is a single layer of hybridized carbon atoms that has attracted attention due to their electronic and structural characteristics. The RGO can act as a support for immobilization of several species, which demonstrates its applicability in different research fields, such as catalysis, energy storage and sensors development. One special substance used as a RGO modifier is the metallic porphyrins (MP). These complexes are well recognized for their excellent electrocatalytic activity for many reactions and can adsorb over RGO surface via  $\pi$ - $\pi$  interactions. It has been observed that MP/RGO composite has the excellent catalytic properties of the MP without losing any of the electronic properties of the RGO. The objective of this work is the synthesis, characterization and application of an electrochemical sensor based on a metallic porphyrin supported on RGO for the electrochemical determination of endocrine disruptor, such as  $17\beta$ -estradiol. The sensors were prepared by a single mixture of 0.5 mg of RGO, 0.5 mg of Cu(II)-meso-tetrathienyl porphyrin (CuTthP) and 1.0 mL of ethanol. This mixture was kept under an ultrason bath for 1 hour. Thus 10 µL of the obtained suspension was dropped over top a glassy carbon (GC) electrode. The FEG-SEM images of RGO presented as a wrinkled paper-like multilayer structure, with the edge thickness of the graphene nanosheets measured in this image is about 1.2 nm. Also the FEG-SEM images of the RGO/Cu-TthP demonstrated that the porphryn was completely attached over the graphene surface, with a characteristic  $\pi$ -stacking attachment. The electrochemical behavior of the 17 $\beta$ -estradiol over GC/RGO/CuTthP surface was carried out using differential pulse voltammetry (DPV) in PBS (pH 7.0) and demonstrated that the 17β-estradiol has an oxidation peak in +0.53 V. The observed value of the current peak increased in almost 3-fold when compared with the sensor fabricated in absence of CuTthP. DPV experiments allowed the development of a method to determine 17β-estradiol levels in the range from 0.1 to 10.0  $\mu$ mol L<sup>-1</sup> with a detection limit of 5.3 nmol L<sup>-1</sup> (1.4  $\mu$ g L<sup>-1</sup>). In conclusion it was developed an efficient electrochemical sensor for determination of hormones in environmental samples.

## Silver nanoparticles-decorated carbon in ionic liquid carbon paste electrode for improved determination of nitrite

Eva Menart, Vasko Jovanovski, Samo B. Hočevar Analytical Chemistry Laboratory, National Institute of Chemistry Hajdrihova 19, SI-1000 Ljubljana, Slovenia eva.menart@ki.si

Nitrite is used extensively in food industry to prevent bacterial growth and oxidative food degradation, mostly in cured meat products, although it has also been found in commercially available vegetables. Nitrite consumption has been linked with several diseases, but most importantly, it has been found to be a precursor in the formation of nitrosamines and aromatic carbocations, well-known carcinogens. Accurate and direct, although simple methods for measuring trace nitrite are therefore highly desirable.

A new carbon paste electrode (CPE) was designed for this purpose; paraffin which is commonly used in preparation of CPE as a binder was replaced by an ionic liquid trihexyltetradecylphosphonium chloride that significantly improved the signal-to-noise ratio and enabled a possible additional interaction (e.g. extraction, ion exchange) with the analyte. The electroanalytical performance of the sensor was further enhanced via decorating carbon particles with silver nanoparticles (AgNPs) using the citrate method. Silver nanoparticles-decorated carbon-based ionic liquid carbon paste electrode (AgNPs-IL-CPE) revealed a considerable electrocatalytic effect upon nitrite oxidation reaction displaying a substantial increase of the signal and the peak potential shift towards less positive potentials for ca. 110 mV. Several carbon/silver ratios were investigated and the AgNPs-IL-CPE composed of carbon powder with added 20 wt.% Ag during modification displayed the most favourable electroanalytical characteristics. Nitrite ion concentration was measured using direct square-wave voltammetric mode and several operational parameters were optimised. Two-step conditioning at -0.5 V and +0.5 V was shown to have a beneficial effect on the signal height, probably via activating the silver-decorated carbon surface. The initial potential of the voltammetric scan also had a profound effect on the electrode performance; starting the scan at -0.5 V significantly increased the signal. Using 0.1 mol  $L^{-1}$  NaCl in 0.1mmol  $L^{-1}$  HCl as the electrolyte provided the most favourable electrode operation indicating a possible effect of the AgCl formation during the conditioning step. In addition, the novel AgNPs-IL-CPE unveiled a good linear response in the examined concentration range of 0.05 to 1.0 mmol L<sup>-1</sup> with an LOD of 3.0 µmol L<sup>-1</sup>, outstanding repeatability (RSD of 0.3 %) and the absence of any memory effect.

# Glassy carbon electrodes modified by supramolecular assemblies of metalloporphyrins. Effect on the method of modification towards hydrogen evolution

Camila Pía Canales and Galo Ramírez\*

Pontificia Universidad Católica de Chile, Facultad de Química, Departamento de Química Inorgánica, Laboratorio de Electroquímica, Av. Vicuña Mackenna, 4860, Macul, Santiago, Chile. E-mail:gramirezj@uc.cl

The modified electrodes with macrocyclic complexes have been widely studied because of its high activity on interesting reactions. Recent investigations on electrocatalysis field, electrode modifications with macrocyclic complexes such as porphyrins or phthalocyanines with metal center, have a great versatility due to its electrochemical activity as electrocatalysts, detectors and sensors in a huge variety of reactions [1,2]. Parallel to this, the supramolecular chemistry is a multidisciplinary field focused on the study and use of molecular assemblies unified through non-covalents interactions. The supramolecular systems formation is a spontaneous process that has no requirement of high activation energies. The loss of the entropy is widely reestablished by the negative variations in the enthalpy due to the formation of a great amount of non-covalent bonds [3,4].

In this work, it is proposed the developing of a new material: a modified glassy carbon electrode with metallic octaethylporphyrins, MxOEP (Mx = Co, Cu, Zn, Ru, Fe and Ni), assembled by  $\pi$  – interactions on a surface previously modified with covalent bonds which have a behavior as a supramolecular system. The covalent bonds are formed by using molecules such as 4-aminopyridine (4AP), isonicotinic acid (IA), 4-aminobenzoic acid (PABA) and by forming oxidized functional groups on the carbon surface (GC-ox). Then, two different methods are done in order to modify the system with metalloporphyrins: by the electrode submersion at room temperature and by reflux at 80°C in the porphyrin solution. It was found that, in all cases, the supramolecular system generated by reflux have greater activity towards hydrogen evolution in comparison to those ones generated by submersion (eg. figure 1a). Also, the best supramolecular system corresponds to the GC-ox modified with Cu(II)OEP, which is more active towards hydrogen evolution (figure 1).

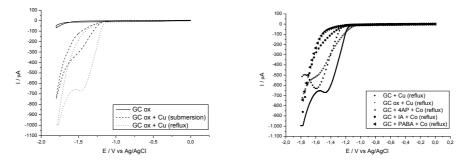


Figure 1. a) Effect on the method of modification: GCE-ox modified with Cu(II)OEP, b) voltammetric response of different modified systems towards hydrogen evolution.

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# MnO<sub>2</sub> – carbon nano-composites prepared by electrospraying as electrodes for supercapacitors

R. Fojtikova<sup>2</sup>, <u>P. Mazur<sup>1</sup></u>, J. Pocedic<sup>1</sup>, J. Dundalek<sup>2</sup>, J. Kosek<sup>2</sup>

 University of West Bohemia, Research Centre - New Technologies, Univerzitní 8, 306 14 Plzeň, Czech Republic mazurp@ntc.zcu.cz
 Institute of Chemical Technology Prague, Dept. of Chemical Engineering, Technická 5, 166 28 Praha 6, Czech Republic Juraj.Kosek@vscht.cz

The electrochemical double-layer capacitors (so called supercapacitors) are promising energy storage devices bridging the gap between the conventional capacitors and batteries. However, in order to extend their application range, the increase in stored capacity is desirable. This may be achieved by the utilization of pseudocapacitive contribution of faradaic processes, e.g. redox reaction, under-potential deposition or ion intercalations[1]. In our contribution the electrochemical properties of MnO<sub>2</sub> - carbon composites were evaluated with respect to its application as electrodes for supercapacitors using aqueous and non-aqueous electrolyte. For the deposition of  $MnO_2$  we selected the optimized method of electrospraying in the high voltage electric field using aqueous solution of manganese acetate as the precursor. This enabled direct deposition of the MnO<sub>2</sub> particles of uniform size distribution in range of tens of nm. The implementation of carbon-based additives into the structure of the layer increased the specific surface area and conductivity of the layer. We tested several methods of the preparation of composite layers: (i) direct electrospraying of suspension containing carbon filler (carbon black, activated charcoal) and MnO<sub>2</sub> precursor, (ii) electrospraying of glucose based precursor of carbon and its subsequent carbonization under inert atmosphere, (iii) deposition of  $MnO_2$  onto the pre-deposited carbon layers. The deposited layers were characterized using SEM, AFM, Raman and XPS. The electrochemical characterization in three-electrode configuration showed the positive effect of pseudocapacitive contribution of Na<sup>+</sup> ion intercalation on the overall capacitance of the prepared layers.

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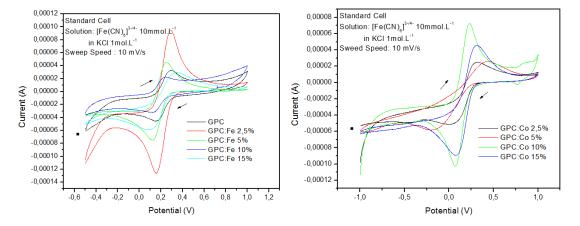
## Synthesis, and Voltammetric Properties of Fe and Co Ions Modified Glassy Polymeric Carbon

L.S. Novais, R. P. de Camargo and H.P. Oliveira

Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto – Departamento de Química – Universidade de São Paulo – Ribeirão Preto –SP – Brazil e-mail: lauranovais@hotmail.com

The electrochemical properties of glassy polymeric carbon (GPC) modified with iron and cobalt ions in bulk phase (GPC:Fe and GPC:Co) were investigated as a function of concentration of these ions (2.5%, 5%, 10% and 15%). More specifically, the GPC electrodes were prepared via pyrolysis of low molecular weight phenol-formaldehyde oligomers that leads to low polydispersity polymer, which enables, after a carefully increase of temperature in nitrogen atmosphere, the formation of a glasslike carbonaceous material. The metallic ions were added by mixing appropriate metal salts dissolved in alcoholic medium with phenol-formaldehyde resin. The resulted modified metallic ion/resin was placed in plastic mold, and cured in an oven at 60 °C for 72 hours in air. Then, the mold was disassembled and the cross-linked polymer was slowly pyrolyzed in a tubular furnace at temperatures ranging from 25 °C to 1200 °C in nitrogen atmosphere. The next step consisted in to assemble carbon paste electrode in a Teflon tube, and the electrical contact was done by copper wire. Cyclic voltammetry of ferrocyanide oxidation/reduction was carried out using Fe and Co ions modified GPC electrodes of different contents of metallic ions. The electroactivity of the modified GPC was clearly demonstrated by cyclic voltammetric measurements. Cyclic voltammetric studies using FeCN<sub>6</sub><sup>3-/4-</sup> system and KCl as electrolyte support solution were carried out using these electrodes, and kinetics parameters (k°, mr e D) were evaluated [1]. Based on voltammograms and by comparing with those obtained with GPC without any modification, one can conclude that the samples GPC:Co presented better kinetic parameters such as electron transfer rate (~10<sup>4</sup>  $cm.s^{-1}$ ) for all speed rates, while electrodes with iron ions has transfer rate around  $10^{-5}$  cm.s<sup>-1</sup>, with exception for the sample with lower amount of iron ions that presented a similar performance when compared with GPC modified with cobalt ions. In contrast, when we consider voltammetric parameters that define the behavior of the electrode for the system investigated, it was observed that the difference between cathodic peak potentical and anodic peak potential as well its ratio [2], the GPC:Fe electrodes, mainly for 2,5% e 5,0%, showed a very close values with those found in the literature. Overall, the voltammograms show that the increase of metallic ions improves the electrochemical response, *i.e.*, values for the standard rate constant,  $k_0$ , increase as the amount of metallic ions into GPC bulk phase rises. Indicating a better electronic transfer process [3].

Acknowledgments : FAPESP and CNPq



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## Voltammetric Properties of Glassy Polymeric Carbon Obtained at Different Synthesis Temperature

L.S. Novais, W.C. Muscelli and H.P. Oliveira

Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto – Departamento de Química – Universidade de São Paulo – Ribeirão Preto –SP – Brazil e-mail: lauranovais@hotmail.com

Among several kinds of carbon electrodes, polymeric glassy carbon based on phenolic resin is particularly attractive as electrode material due to its thermal stability, robustness, mechanical strength, electrical conductivity and large potential range [1,2]. As these carbon-based materials are prepared at low temperature (approximately 1000 - 1500 °C), some kilning faults can be arisen leading to changes in electrochemical behavior. Thus, in order to overcome this drawback, low molecular weight phenolformaldehyde oligomers were first synthesized resulting in a low polydispersity polymer, which enables, after a carefully increase of temperature in nitrogen atmosphere, the formation of a glasslike carbonaceous material. In this context, electrochemical properties of polymeric glassy carbon monoliths were investigated in function of different synthesis temperature. The GPC was prepared from a viscous light yellow phenol-formaldehyde resin, which presents low polydispersity index value (PD = 1.11), estimated by means of weight-average mass and number-average molar mass obtained from Gel Permeation Chromatography. After curing the resin in an oven at 60 °C, which was previously placed in a plastic mold, the thermosetting polymer has a well-shaped form; as well as it presents a dense structure. Subsequently, the mold was disassembled and the cross-linked polymer was thermally treated up to 1650 °C in nitrogen atmosphere. As a result, the final material is a nonporous glasslike solid that is conductive and it has a rigid structure. Afterwards, homemade electrodes were confectioned with Teflon mold, and felt carbon was used for electric contact. The influence of high temperature treatment (750 °C, 950 °C, 1100 °C, 1300 °C, and 1650 °C) on polymeric glassy carbon structure was investigated and correlated to electrochemical parameters obtained from cyclic voltammetry technique. Besides, it was investigated how the surface organic groups affect the kinetic parameters such as both electronic and mass transfer coefficients as well as diffusion coefficient. Defects are decreased as temperature increase, which is verified by roughness coefficient estimated from atomic force microscopy technique. The GPC obtained at 750 °C has the higher average value (1405 nm) and the values decrease as the thermal temperature increases, thus for the sample treated at 1650 °C the roughness coefficient is 553 nm. Therefore, surfaces with lower coefficients present minor active surface area [3], and, as a consequence, a double layer capacitive effect is decreased as verified by the voltammetric profiles. Cyclic voltammetric studies using  $FeCN_6^{3-/4-}$  system and KCl as electrolyte support solution were carried out using these electrodes of different temperature treatment (TT). The voltammograms showed how the ferrocyanide kinetics improve with increasing the TT and that the peak current were found to be linear with the square root of the scan rate for all electrodes. Besides, the kinetics parameters [4] such as k°, m<sub>r</sub> and D ( $\approx 9.10^{-5}$  cm.s<sup>-1</sup>, 2.10<sup>-8</sup> cm<sup>2</sup>.s<sup>-1</sup> and 9.10<sup>-5</sup> cm.s<sup>-1</sup> at 10 mV/s) of the polymeric glassy carbon obtained at temperature above 1100  $^{\circ}$ C were quite similar to those obtained from Metrom GC 20 mm commercial electrode (4.01.10<sup>-6</sup> cm.s<sup>-1</sup>,  $2.10.10^{-9}$  cm<sup>2</sup>.s<sup>-1</sup> and  $2.86.10^{-5}$  cm.s<sup>-1</sup>). For voltammetric application, glassy carbon samples heat-treated to 1300 °C and 1650 °C are the most appropriate due to the electrolyte background currents are lower over potential range.

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## **Electrochemical Reduction of Nitrate Using Boron-Doped Nanocrystalline Diamond Grown on Reticulated Vitreous Carbon**

<u>Silvia Sizuka Oishi<sup>1</sup></u>, Andrea Boldarini Couto<sup>1</sup>, Edson Cocchieri Botelho<sup>2</sup>, Mirabel Cerqueira Rezende<sup>3</sup>, Maurício Ribeiro Baldan<sup>1</sup>, Neidenêi Gomes Ferreira<sup>1</sup>

<sup>1</sup>Instituto Nacional de Pesquisas Espaciais (INPE), São José dos Campos, 12227-010, Brazil <sup>2</sup>Department of Materials and Technology, UNESP-Univ. Estadual Paulista, Guaratinguetá, São Paulo, 12516-410, Brazil <sup>3</sup>Institute of Science and Technology, UNIFESP-Univ. Federal de São Paulo, São José dos Campos, São

Institute of Science and Technology, UNIFESP-Univ. Federal de Sao Paulo, Sao Jose dos Campos, Sao Paulo, 12231-280, Brazil

silviaoishi@uol.com.br

The worldwide problem in good quality water demand, due to an increase in consume and decrease in water resources, requires a continuous search for new materials and technologies for polluted water treatment. The nitrogen compounds arising from agriculture and from some industrial sectors are among the contaminants, which in the environment represent a health risk. One of the most efficient and promising materials for electroreduction are the boron-doped diamond electrodes, due to a good response in reduction of compounds that are difficult to reduce, like the nitrate. However, the diamond properties may depend on different experimental conditions such as the substrate used in diamond growth and the doping level. This work investigates the use of reticulated vitreous carbon (RVC) and RVC/boron-doped nanocrystalline diamond (RVC/BDND) composites as electrodes for nitrate reduction. RVC was processed using poly(furfuryl alcohol) resin synthesized according to the best condition established previously (1). Polyurethane foam with 70 ppi (pores per inch) was used as matrix for the PFA.anchorage. Nanocrystalline diamond films were grown by hot filament chemical vapor deposition (HFCVD) technique, using 5 filaments of tungsten with 125 µm diameter, placed at 6 mm of sample top and 18 h of deposition time. Reactor pressure and the substrate temperature were kept at 4 kPa and 670 °C, respectively, with a gas mixture composed by 70.8% Ar, 28.3% H<sub>2</sub> and 0.88% CH<sub>4</sub>. The boron doping was performed by an additional hydrogen line passing through a bubbler containing  $B_2O_3$  dissolved in CH<sub>3</sub>OH. The solution was prepared with a concentration of B<sub>2</sub>O<sub>3</sub> dissolved in CH<sub>3</sub>OH that correspond to B/C ratio of 30,000 ppm. Electrochemical measurements were carried out with a Potentiostat Autolab PGSTAT 302 using solutions of 0,1 mol L<sup>-1</sup> of K<sub>2</sub>SO<sub>4</sub> + 150 ppm KNO<sub>3</sub> RVC and RVC/BDND were used as cathode and boron-doped diamond grown on titanium as anode. RVC/BDND presented the best result with a nitrate reduction of 95.2% comparing to 59.3% reached by RVC after 5h. However, the generation of by-products such as NO<sub>2</sub><sup>-</sup> and NH<sub>3</sub> during the cathodic reduction of nitrate is still a problem and appropriate experimental conditions should be investigated.

Acknowledgements: FAPESP, CAPES and CNPq (Brazil).

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## The Influence of the Adsorption Sites Electronic Structure on CO Poisoning Process at Ordered Intermetallic Surfaces

<u>A.C.D. Ângelo<sup>1</sup></u>, A.C. Garcia<sup>2</sup> and F. Bortoloti<sup>1</sup> <sup>1</sup>Electrocatalysis Laboratory, UNESP. <sup>2</sup>Electrochemistry Laboratory, IQSC, USP. Chemistry Dept., PO Box, 473, Bauru, SP, 17033-360, BRAZIL. acangelo@fc.unesp.br

One of the most important constraints to be overwhelmed to become the hydrogen fed Fuel Cell an actual source of energy in a sustainable development concept is the use of the fuel obtained from the catalytic reforming process of biomass derived products. Even though this is a very inexpensive process in comparison to the electrolysis product, the crucial problem is the co-production of CO as contaminant. The usual approach to achieve electrode materials less susceptible to CO poisoning is the addition of oxophilic transition metals to the structure of the noble metals. The result of such procedure is commonly ascertained to one or more of the following causes: A-third body effect; B-early formation of oxidized species (bifunctional effect); C- electronic effect (electrocatalytic). The present study has investigated the electronic structure of Pd and Pt adsorption sites, modified by Sn insertion in the ordered intermetallic geometric one and its influence on the hydrogen oxidation reaction on CO-poisoned surfaces.

Ordered intermetallic PdSn and PtSn anchored on Carbon were synthesized from the corresponding Chloride salts reduction via a modified polyol route. The obtained PdSn/C and PtSn/C were characterized by X-Ray Diffraction; Energy Dispersion X-Ray Spectrometry, Transmission Electron Microscopy and X-Ray Absorption Spectroscopy techniques. The electrochemical activity and kinetics towards the Hydrogen Oxidation Reaction were investigated in 0.2 mol.L<sup>-1</sup> KOH solution by using Rotating Disc Electrode technique at the clean and deliberately CO-poisoned surfaces. All potentials herein cited is referred to the Reversible Hydrogen Electrode.

The PdSn/C and PtSn/C materials were doubtless characterized as ordered intermetallic materials crystalized in orthorhombic and hexagonal structures respectively. No impurity detected by the technique was observed. The composition were determined by EDS as 1:1 (Noble metal : Tin) and a very low dispersion was detected. The nanoparticles sizes were estimated from TEM measurements as about 2nm for both materials.

At clean surfaces, PdSn/C has showed an 200mV overpotential for the HOR as compared to PtSn/C, however, they were determined the same value for the kinetic current density equals to 267 mA.mg<sup>-1</sup><sub>Pd,Pt</sub>. On the other hand, at CO-poisoned surfaces, while the reaction taking place on PtSn/C showed splitted waves corresponding, probably, to the reaction occurring on two different adsorption sites (where one of them showed a remarkable influence of the CO-poisoning); the waves has been almost completely suppressed on CO-PdSn/C. Under such conditions, PtSn/C has achieved a kinetic current density of 130 mA.mg<sup>-1</sup><sub>Pt</sub> and for PdSn/C the value determined was 33 mA.mg<sup>-1</sup><sub>Pd</sub>. Moreover, the charges involved in the CO-stripping process were 67 and 4900  $\mu$ C respectively for PtSn/C and PdSn/C ordered intermetallic materials. It was experimentally supported that PtSn/C is far less susceptible to CO-poisoning than PdSn/C and that CO-PtSn/C still presents a reasonable activity towards the HOR.

It is well known and accepted that Sn exerts an electron donor effect towards Pt orbitals, increasing the electron density of Pt ( $[Xe] 4f^{14}5d^96s^1$ ) adsorption sites. This action is particularly effective in Pt sites since the half-filled d-orbitals favor the phenomenon. On the other hand, the electronic configuration of Pd ( $[Kr] 4d^{10}$ ) does not ease the donor action from Sn ( $[Kr] 4d^{10}5s^25p^2$ ) atoms since the Pd d-orbitals are already filled. In parallel, the character oxophilic of Sn atoms at the noble metals surfaces will always be present and, as a consequence, oxygenated species (-OH, -OOH, -O<sub>2</sub>) will be produced at the materials surfaces at less positive electrode potentials in comparison to the pure noble metals. Based on the above presented presumed characteristics, it is supposed that the electronic effect will preferentially take place at PtSn surface while the bi-functional effect may be prevalent at PdSn surface. XAS experiments has proved that there is an effective increase of the electronic density of the Pt adsorption site that became it less susceptible to the CO-poisoning effect.

In conclusion, it was attested the promising characteristic of PtSn/C ordered intermetallic material as electrocatalyst for the HOR as the cell is fed as Hydrogens gas contaminated with CO.

## Acknowledgements: FAPESP, CNPq, CAPES, POSMAT, LNLS.

# **Evaluation of a Glassy Carbon Electrode Modified with Printex 6L Carbon Black for the Development of Electrochemical Sensors**

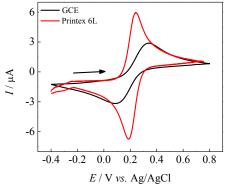
<u>Geiser G. Oliveira<sup>1,\*</sup></u>, Laís S. Pereira<sup>2</sup>, Bruna C. Lourenção<sup>2</sup>, Fernando C. Vicentini<sup>2</sup>, Marcos R. V. Lanza<sup>1</sup>, Orlando Fatibello-Filho<sup>2</sup>

<sup>1</sup>Institute of Chemistry of São Carlos, University of São Paulo, São Carlos – SP, Brazil <sup>2</sup>Department of Chemistry, Federal University of São Carlos, São Carlos – SP, Brazil \*geisergabriel@gmail.com

Carbon black (CB) is applied as an electrically conductive filler in polymer-matrix composites as electrogeneration of hydrogen peroxide in gas diffusion electrode<sup>1</sup>, in fuel cells and lithium batteries<sup>2</sup>. Those use calls our attention to development of electroanalytical sensors for applications for the determination of analytes of interest in several matrix. In this context, we explore a type of carbon black as electrode material towards commonly encountered redox probe in aqueous solutions; thus providing information on the electronic properties and applicability of this intriguing material.

The morphological study was carried out by SEM and the electrochemical characterisation of Printex 6L carbon black, was performed towards the well characterised inner-sphere redox probe  $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$  redox probe in 0.1 mol L<sup>-1</sup> KCl electrolyte.

The glassy carbon electrode (GCE – 3.0 mm in diameter) was modified with Printex 6L (Degussa from Brazil Ltda) dispersion. Before the modification, the GCE was polished successively with alumina on a polishing cloth and then rinsed with ultra-pure water and 2-propanol. Next, the Printex 6L dispersion was prepared by dispersing 1.0 mg Printex 6L in 1.0 mL of ultrapure water, and was placed under ultrasonic agitation for 20 minutes. Then, 8  $\mu$ L of the Printex 6L dispersion was dropped onto the GCE surface and the solvent allowed evaporating at 25 °C for 2 h.



In Fig. 1 it is shown typical voltammograms for Printex6L/GCE (–) and GCE (–) at a scan rate of 50 mVs<sup>-1</sup> exhibits a well-defined pair of redox peaks with a peak separation ( $\Delta E_p$ ) of ca. 56.0 and 256.0 mV (*vs.* Ag/AgCl (3.0 mol L<sup>-1</sup> KCl)), respectively. The Printex 6L present a smaller  $\Delta E_p$  value than that exhibited by GCE, which is an indicative of a more favourable electrochemical interaction at the electrode surface and thus enhanced electron transfer kinetics, obtaining a value of  $7.0 \times 10^{-4}$  and  $1.2 \times 10^{-1}$  cm s<sup>-1</sup> for GCE and Printex 6L, respectively.

With the incorporation of the Printex 6L film onto the GCE surface, the analytical signal was substantially increased and a decrease in the oxidation and reduction potentials was obtained, a characteristic of the electrocatalytic effect. Furthermore, the use of Printex 6L film showed an increase in the oxidation current of 94% and in the reduction current of 121%.

The electroactive surface area was also calculated for both electrodes using the Randles–Sevcik equation and the obtained values were  $0.053 \text{ cm}^2$  for GCE and  $0.087 \text{ cm}^2$  for Printex 6L, respectively, an increase of 64%.

This work demonstrates the potential of Printex 6L as electrode material in the electrochemistry, in terms of electron transfer kinetics and the magnitude of the analytical signal.

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## Novel class of interconnected carbon nanospheres

Hudson Zanin<sup>1</sup>\*, A. C. Peterlevitz<sup>2</sup>, Paul W May<sup>3</sup>, R. Harniman<sup>3</sup>, Vitor Baranauskas<sup>2</sup> and David Fermin<sup>3</sup>

<sup>1</sup> Laboratory of Biomedical Nanotechnology / Institute of Research and Development at UNIVAP, Av. Shishima Hifumi, 2911, CEP: 12244-000, Sao Jose dos Campos, SP, Brazil.

<sup>2</sup> Faculdade de Engenharia Elétrica e Computação, Departamento de Semicondutores, Instrumentos e Fotônica, Universidade Estadual de Campinas, UNICAMP, Av. Albert Einstein N.400, CEP 13 083-852 Campinas, São Paulo, Brazil

<sup>3</sup> School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, United Kingdom.

## e-mail address hudsonzanin@gmail.com

Novel hydrophilic carbon nanospheres with average crystallite size of  $\sim 5$  nm and composed of laminar graphene layers separated by interplanar spacing of  $\sim 0.32$  nm were deposited onto a niobium substrate by hot filament chemical vapour deposition. To prepare a thin-film of interconnected carbon nanospheres (ICNSs), solvent-refined oil without additives was annealed up to  $530^{\circ}$ C under 20 torr of a gas mixture containing ethanol, methanol, water, and boron trioxide, conditions. The resulting thin film was characterized by scanning and transmission electron microscopy, Raman, Fourier transform infrared and energy dispersive spectroscopies. The film behaviour as an electrochemical electrode was studied by cyclic voltammetry and electrochemical impedance spectroscopy. ICNS layers exhibit large potential window, low uncompensated resistance, as well as low charge-transfer impedance in the presence of ferrocene-methanol or ferrocyanide as redox probes. These useful properties make ICNS electrodes very promising for future applications in electrocatalysis and (bio)sensors.

Keywords: graphene sheet, laminar graphene sphere, fast electron transfer, wettability, hydrophilicity

# Preparation and Characterization of Cyclodextrin Modified Graphene Oxide for Molecular Recognition Mediated by Host-Guest Interaction

<u>Claudia Yáñez<sup>1</sup></u>, Elias Villalobos<sup>1</sup>, José F. Marco<sup>2</sup> <sup>1</sup> Facultad de Ciencias Químicas y Farmacéuticas. Universidad de Chile. Casilla 233. Santiago. Chile. 2 Instituto de Química Física "Rocasolano". CSIC. Madrid cvanez@cig.uchile.cl

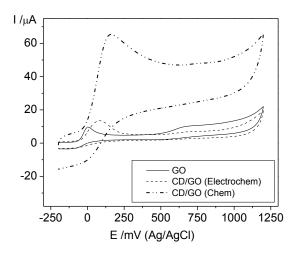
Modification of surfaces is very important for applications in detection and analysis. It is expected that the surfaces covered with host molecules show the ability to bind diverse molecules from aqueous solution by molecular recognition. Attachment of host molecules on surfaces remains an important research topic within electroanalytical techniques. Based on the encapsulating properties of cyclodextrins (CDs), they are an attractive group used as modifier of surfaces. CDs are cyclic oligosaccharides composed of six, seven, or eight glucose units ( $\alpha$ -,  $\beta$ -, or  $\gamma$ -CD, respectively), which are toroidal in shape with a hydrophobic inner cavity and a hydrophilic exterior. Thus, they can be used to bind selectively organic molecules of hydrophobic nature into their cavities to form stable host-guest inclusion complexes, showing high molecular selectivity.

In the present work, we have prepared CD modified graphene oxide and we have studied its behavior towards ascorbic acid. Graphene oxide (GO) and heptakis-(6-amino-6-deoxy)- $\beta$ -CD (CD-NH<sub>2</sub>) were used. Two simple routes for the preparation of cyclodextrin modified graphene oxide (CD/GO) are presented: (i) direct electro-oxidation of amine groups presents in  $\beta$ -CD on GO/glassy carbon electrode (electrochemical method), and (ii) covalent bond of CD-NH<sub>2</sub> using ethilcarbodimide (EDC) and N-hidroxisulfosuccinimide (NHS), (chemical method). A dispersion is prepared with this product and deposited on glassy carbon surface using a drop coating method. The modified electrodes have been characterized by using X-ray photoelectron spectroscopy (XPS) and the electrochemical response towards two electroactive probes such as ferrycianide and ferroceno redox couples.

The N1s deconvoluted spectrum obtained by XPS can be curve-fitted into three peak components with binding energy of 397.7, 399.03 and 401.02 eV which may be assigned to the C-N amide or amine components, and the charged quaternary nitrogen species, respectively, confirming in this way the bond of CD with graphene oxide. Based on the XPS results, the C1s, O1s and N1s peak areas for CD/OG (electrochemical method) was determined, providing a quantitative measure of the extent of functionalization. The concentration of carbon,

oxygen and nitrogen are 48.5, 48.0 and 3.5 atomic %, respectively.

The electro-oxidation of ascorbic acid have been used to evaluate both two preparation routes. One oxidation peak is observed at 2.8 mV on GO (figure, solid line). When CD/GO is used, the respective peak potential moves towards higher positive potential values (85 and 160 mV). Moreover, the current is almost 5 times higher when CD/GO (chemical method) is used. The changes in the ascorbic acid oxidation current and potential are attributed to the formation of the surface inclusion complex (host-guest interaction), provoking a strong adsorption of ascorbic acid on the modified surface. Therefore, this surface could be adequately used for electrochemical quantification.



#### Acknowledgements

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# Study of the oxygen reduction reaction on carbon black modified with Nb-Ru binary oxides

Ricardo B. Valim<sup>2</sup>, Robson S. Rocha<sup>1</sup>, Geiser G. Oliveira<sup>2</sup>, Jussara F. Carneiro<sup>2</sup>, Fernando Lindo<sup>2</sup>, Marcelo Zaiat<sup>1</sup>, Marcos R. V. Lanza<sup>2</sup>\*

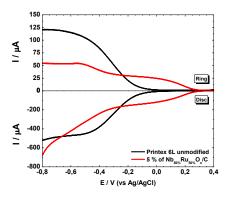
1 - Escola de Engenharia de São Carlos – Universidade de São Paulo

2 - Instituto de Química de São Carlos – Universidade de São Paulo

Av. João Dagnone, 1100, CEP 13563-120, São Carlos, SP, Brasil \*marcoslanza@iasc.usp.br

## Abstract

In the interest of studying the electrogeneration of hydrogen peroxide from oxygen reduction reaction (ORR) were added Nb and Ru metals in the mass ratio of 5% of metal to the total carbon Printex 6L (Degussa Brazil Ltda), and the synthesis of oxides of the respective metals were made by Pechini modified method. The study of the ORR was made by Linear Voltammetry using a solution of 0.1 mol  $L^{-1}$  K<sub>2</sub>SO<sub>4</sub> (pH 2.0) as electrolyte and rotating ring-disc electrode (RRDE) with the studied material deposited on the surface of the disk by porous microlayer technique. The experiments were performed with control of rotation of the work electrode, at rotational of 900 rpm.



**Figure 1**: Linear voltammogram of Printex 6L and 5% Nb<sub>0,5</sub>Ru<sub>0,5</sub>O<sub>x</sub>/C in the potential range of +0.4 V to -0.8 V (vs. Ag/AgCl) with a scan rate of 5 mV s<sup>-1</sup>, supporting electrolyte of 0.1 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> (pH 2.0) and saturated with O<sub>2</sub> gas flow of 1 mL min<sup>-1</sup> for both experiments.

In Figure 1 is shown the results obtained for the Printex 6L carbon materials without modifier and 5%  $Nb_{0,5}Ru_{0,5}O_x/C$  in rotation speed of 900 rpm. The offset for more positive potentials of the beginning of the RRO is interesting for the application of the studied material in the confection of gas diffusion electrodes, favoring electrogeneration hydrogen peroxide in measurable scale, with possible utilization of lower energy electrogeneration.

ACKNOWLEDGMENTS

FAPESP, CNPq and CAPES for financial support.

# Ordering Effect on the Electroactivity of Noble Metals Intermetallics Toward Glycerol Eletrooxidation Reaction.

<u>K.Barrezzi<sup>1</sup></u>, F.Bortoloti<sup>1</sup>, J.P. Garcia<sup>1</sup>, A.C. Garcia<sup>2</sup> and A.C.D Angelo<sup>1</sup> <sup>1</sup>Electrocatalysis laboratory, FC, UNESP. <sup>2</sup>Electrochemistry Laboratory, IQSC, USP Chemistry Dept., UNESP, PO Box 473, 17033-360, Bauru, SP, Brazil. ka barrezzi@yahoo.com.br

It is an usual approach using intermetallics materials in order to improve the alcohols electrooxidation reaction by a combination or one of the following actions: A-Third body effect; B-Bifunctional action; C-Electronic modification of the adsorption surface sites. Even though this approach has carried out an undeniable development of the electrocatalysis in the alcohol electrooxidation reactions, it is still unclear the mechanism of such improvement, since the addition of a second metal to a matrix of a noble metal causes both: the electronic and geometric modifications.

This paper presents a contribution to the understanding of geometric/electronic effects in the electrode reaction of glycerol oxidation by investigating the effect of the ordering of crystal nanoparticle material on the electrode reaction. For this, it was employed different catalysts crystalized both as alloy and as ordered intermetallic material.

AuSn/C and PtSn/C nanoparticles were synthesized via modified polyol (ordered intermetallic) or microemulsion (alloy) methods. The obtained products were characterized by X-Ray Diffraction (DRX), Energy Dispersive Spectrometry (EDS) and X-Ray Absorption Spectroscopy (XAS) techniques. Cyclic voltammetry (VC) was employed to observe surface modification caused by the imposed electrode potential as well as to achieve a preliminary evaluation of the material performance as anode. Electrochemical measurements were carried out in 0.2 mol.L<sup>-1</sup> KOH solution and the glycerol was used in a concentration 0.5 mol.L<sup>-1</sup>. All potential in this work are referred to the Reversible Hydrogen Electrode (RHE).

The obtained materials were doubtless identified as AuSn/C alloy; Au<sub>9</sub>Sn/C cluster; PtSn/C alloy and PtSn/C ordered intermetallic, in 1:1 compositional proportion.

In Table I are joined the electrochemical parameters collected for the glycerol electrooxidation reaction in potentiodynamic and steady state experimental condition. For Au nanoparticles it was not possible to observe a clear ordering effect on the performance of the materials as anode for the glycerol oxidation reaction since a surface activation took place probably due to the formation of surface oxidized species. On the other hand, for Pt nanoparticles it was observed a remarkable improvement of the performance for ordered intermetallic material in comparison to the same composition metal alloy.

X-Ray Absorption Near Edge Structure (XANES) analysis has provided the information that the electronic donation action of Sn atoms toward Pt atoms is more effective in the ordered intermetallic structure than in the alloy one, which may be the responsible for the remarkable performance of the ordered intermetallic material.

Analysis of the products of the glycerol electrooxidation on the different materials is being currently performed to investigate the effect of the crystal ordering on the mechanism of the reaction.

Material	Cyclic Voltammetry			Chronoamperometry	
	OP (V)	jp (mA mg <sub>Au ou Pt</sub> -1)	Ep (V)	jp (mA mg <sub>Au ou Pt</sub> -1)	Ер (V)
AuSn/C alloy	0,84	806	1,39	69	1,24
PtSn/C alloy	0,53	156	0,76	5	0,57
Au <sub>9</sub> Sn/C cluster	0,89	366	1,30	64	1,23
PtSn/C ordered intermetallic	0,54	1113	0,91	54	0,81

Table I: Electrochemical parameters obtained from potentiodynamic and steady-state techniques.

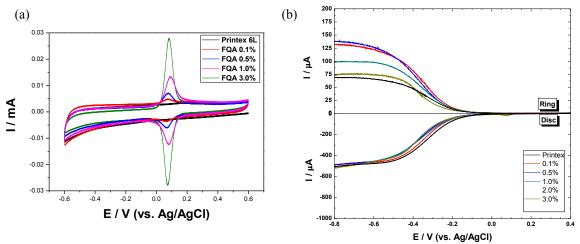
Acknowledgments: FAPESP, CNPq, CAPES and POSMAT.

# Study of the oxygen reduction reaction on carbon black modified with 9,10-Phenanthrenequinone

<u>Fernando Lindo Silva<sup>1\*</sup></u>, Matheus S. Kronka<sup>1</sup>, Marcos R. V. Lanza<sup>1</sup> <sup>1</sup>Instituto de Química de São Carlos – Universidade de São Paulo Av. João Dagnone, 1100, CEP 13563-120, São Carlos, SP, Brasil \*fernandolindosilva@gmail.com

## <u>Abstract</u>

In the interest of studying the electrogeneration of hydrogen peroxide from oxygen reduction reaction (ORR) were added 0.1, 0.5, 1.0 and 3.0% w/w of 9,10-Phenanthrenequinone (FQA) to Printex 6L carbon (Degussa). The study of the ORR was made by linear sweep voltammetry using 0.1 mol  $L^{-1}$  K<sub>2</sub>SO<sub>4</sub> (pH 2.5) and rotating-ring disc electrode (RRDE) by porous microlayer method<sup>1</sup>. The experiments were performed at 900 rpm. The FQA characterization was performed using cyclic voltammetry studies<sup>1</sup>.



**Figure 1.** (a) Cyclic voltammogram of Printex 6L and 0.1, 0.5, 1.0 and 3.0% w/w of FQA in the potential range of +0.6 V to -0.6 V (*vs* Ag/AgCl) with a scan rate of 10 mV s<sup>-1</sup>. (b) Linear voltammogram and 0.1, 0.5, 1.0 and 3.0% w/w of FQA in the potential range of +0.4 V to -0.8 V (*vs* Ag/AgCl) with a scan rate of 5 mV s<sup>-1</sup>. Both experiments were performed in supporting electrolyte of 0.1 mol L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> (pH 2.5).

In Figure 1 is shown the results obtained for the Printex 6L carbon materials without modifier and 0.1, 0.5, 1.0 and 3.0 w/w of FQA. In Figure 1 (a) there is a increase in the oxidation/reduction peak with increasing percentage of FQA. In Figure 1 (b), in rotation speed of 900 rpm, we observed an increase in ring current values, this is interesting for the application of the studied material in the confection of gas diffusion electrodes, favoring electrogeneration hydrogen peroxide in measurable scale. Current efficiencies obtained were 84.8% for Printex modified with 0.5% of FQA.

## ACKNOWLEDGMENTS

FAPESP, CNPq and CAPES for financial support.

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# Electrochemical determination of the diffusion coefficient of biological active naphthoquinones in organized medium

<u>Abel I. Balbín Tamayo</u><sup>a,b</sup>, Veronica Barbosa Mazza<sup>b</sup>, Andrea R. da Silva<sup>b</sup>, Ricardo Q. Aucêlio<sup>b</sup>, Ana Margarita Esteva Guas<sup>a</sup>, Pércio Augusto Mardini Farias<sup>b</sup>, Aurora Pérez Gramatges<sup>b</sup> <sup>a</sup>Departamento de Química Analítica, Facultad de Química, Universidad de La Habana, Cuba <sup>b</sup>Departamento de Química, Pontificia Universidade Católica do Rio de Janeiro, Brasil e-mail: aurora@puc-rio.br

Naphthoquinones are bioactive compounds found in many natural sources that can present biologic activities such as anti-inflammatory, analgesic, antineoplastic and trypanocidal. These compounds have been previously quantified using organized surfactant systems to enhance their fluorescence quenching effect on 3-mercaptopropionic acid-CdTe quantum dots (3MPA-CdTe QDs) [1]. The use of these organized assemblies can also bring significant advantages for electroanalytical measurements, such as in the use of microelectrodes to determine the diffusion coefficient of surfactants [2]. In the present work, voltammetry has been employed to access information on the diffusion coefficient (D) of a series of natural naphthoquinones: lapachol,  $\beta$ -lapachone,  $\alpha$ -lapachone and  $\beta$ -lapachone-3-sulfonic, in three different organized surfactant systems (CTAB, SDS, Triton X-100). The method was based on the use of home-made graphite epoxy-resin electrode for the determination of the electroactive species in aqueous organized surfactant systems. The diffusion of naphthoquinones in this type of media is determined by their relative hydrophobicity (most of these compounds present low solubility in water) and its preferential location in surfactant environments with different micropolarity. The micellar self-diffusion coefficient was calculated from the limiting current for the electron transfer of micelle-bound naphthoquinone at the critical micelle concentration, i.e. where the interaction between the micelles is negligible. In the present work, the diffusion coefficient values were determined as a function of the experimental variables for each organized media. Other parameters were also calculated, including the micellar hydrodynamic radius and the aggregation number. The results showed the possibility of determination of these compounds in aqueous micellar solutions, and are useful to explain the improvement in analytical signals in other methods involving organized assemblies.

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# A comparative study of electrochemical performance of graphite, modified graphite and graphene oxide - epoxy resin electrodes as transducers for biosensor applications

<u>Abel I. Balbín Tamayo</u><sup>a,b</sup>, Aurora Pérez Gramatges<sup>b</sup>, Ana Margarita Esteva Guas<sup>a</sup>, Pércio Augusto Mardini Farias<sup>b</sup>

<sup>a</sup>Departamento de Química Analítica, Facultad de Química, Universidad de La Habana, Cuba <sup>b</sup>Departamento de Química, Pontificia Universidade Católica do Rio de Janeiro, Brasil e-mail: ibrahimaries009@gmail.com

Carbon electrodes have been widely used in practical applications, exhibiting a wide range of electron transfer rates for benchmark redox systems, depending on carbon material and surface history. Given the complexity of carbon structures, and the differences in the composition of carbon composites, the question arises as to how such differences and complexity can affect their electrochemical reactivity. For example, graphene has already demonstrated great potentials in various novel sensors which utilize graphene's exceptional electrical properties (e.g., extremely high carrier mobility and capacity), electrochemical properties (e.g., high electron transfer rate), optical properties (e.g., excellent ability to quench fluorescence), structural properties (e.g., one-atom thickness and extremely high surface-to volume ratio), or its mechanical properties (e.g., outstanding robustness and flexibility) [1]. Cyclic voltammetry has been the electrochemical technique of choice for the evaluating the kinetics of electrode reactions for more than four decades [2]. The aim of this work was to prepare and characterized three carbon composite electrodes, and to compare their electrochemistry response, to be used as transducers for biosensor applications. Three kinds of electrodes were comparatively investigated as transducers for biosensors; namely, graphene oxide (GO)/epoxy resin, modified graphite/epoxy resin, and graphite/epoxy resin. The composite electrodes were characterized using scanning electron microscope (SEM), highresolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and a variety of electrochemical techniques, using  $Fe(CN)_6^{3/4-}$  as redox standard reaction. The rate of electron transfer between the electrode surface and the redox system was discussed in terms of the heterogeneous electron transfer rate constant. The results clearly show that the characteristics of the carbon composite have a significant influence in the electrode properties, allowing their use as transducers in the assembly of biosensors. The electrodes obtained in this study showed promissory characteristics for use in analytical sensing molecule biomarkers of viral diseases.

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# Control of the Properties of the Graphene Layers Produced from the Electrochemical Exfoliation of Low Cost Graphite Materials

J.R. Garcia, R.T. Ferreira, F.S. dos Santos, G.Marcinuk, A.V. Pedroso, A.B-H. Bischof, R.B. Estevam,

K.C.C.W.S. Klider, C.A. Pessoa, S.R. Lazaro, K. Wohnrath

Department of Chemistry, State University of Ponta Grossa. 4748, Gal. Carlos Cavalcanti Av., Ponta Grossa – PR, ZP- 84030-900, Brazil.

jrgarcia@uepg.br

Graphene and graphene oxide have received a lot of interest from the scientific community because of their properties as: high mechanical strength, high electrical and thermal conductivity, optical transparence, luminescence, high surface area and good chemical reactivity. Nowadays, there are several methodologies for the preparation of graphene and graphene oxide that use different sorts of graphite. Electrochemical exfoliation is a promising strategy for the preparation of graphene, however the complete control of the quality of the material obtained by this methodology have been not reached, specially concerning the use graphite with less crystallinity and/or purity as starting material. Here, we described the development of a methodology to prepare Graphene Layers by electrochemical exfoliation of carbon rods extracted from spent Zinc-carbon batteries trying to control the grade of graphenezation and defects controlling parameters like applied potential, composition of the electrolyte solution, time and temperature. The characterization of the obtained materials was performed by Raman Spectroscopy (Raman), FT-IR Spectroscopy (FT-IR), Diffuse Light Scattering (DLS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Zeta Potential (ZP). The DLS and ZP analysis demonstrated sizes particles in the order of 100-100.000 nm ZP value about -0,033 V. TEM (Fig.1) and SEM images showed the products of electrochemical exfoliation are compounds by mono and few oxide graphene layers. FT-IR demonstrated characteristics bands of hydroxyl, carbonyl, multiples ring substituted and methylene groups. The D/G (related with defects of the material) and 2D/G (related to grafenization degree, the degree of interlamelar separation) relationship demonstrated that occur an exponential dependence of defects over grafenization degree. The Raman showed that relationship between D/G and 2D/G bands were respectively D/G = 0.56 and 2D/G = 0.73. Reductions reactions were performed with NaOH and ascorbic acid (AA). Observed a improvement in the relationship D/G and 2D/G of 40% and 7,7%, respectively for NaOH. The reduction with AA the improvement to the D/G and 2D/G relationships were 40,5% and 335,6%. The low cost route of graphene oxide preparation with alternative carbon waste source by electrochemical exfoliation demonstrated to be able to produce high quality few layers graphene particles. In the present work, was demonstrated which is possible, from waste carbon source, to prepare high quality graphene oxide and reduced graphene oxide at low cost. This material needs be purifying and the purification method has high efficient degree.

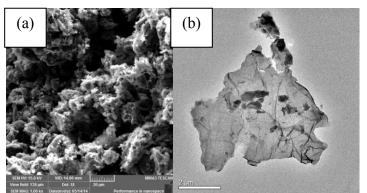


Figure 1: (a) GO particles FEG image and (b) GO a single graphene TEM image.

Acknowledgments: This work was supported by UEPG, Fundação Araucária, CAPES and CNPQ. The TEM was realized in the Central Laboratory of Microscopy - UFSC, Florianópolis – SC, Brazil.

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# Simultaneous Detection of Noradrenaline, Acetaminophen, Xanthine and Theophylline at a Sensor Based on a Graphene Oxide and *o*-Dihydroxy Catechol Modified Glassy Carbon Electrode

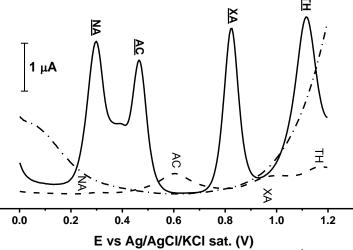
A. William O. Lima<sup>a</sup>, <u>Othon S. Campos<sup>a</sup></u>, Rafael M. Buoro<sup>a</sup>, Jairo J. Pedrotti<sup>b</sup>, Sérgio H. Domingues<sup>b</sup>,

Silvia H. P. Serrano<sup>a</sup>

a - Laboratório de Bioeletroanalítica e Bioeletroquímica, Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo; Av. Prof. Lineu Prestes, 747, B2 S, sala 273, 05508-000, São Paulo, SP, Brasil; b - Escola de Engenharia, Universidade Presbiteriana Mackenzie, Rua Consolação 896, 01302-907, São Paulo, SP, Brasil.

othon@iq.usp.br

Glassy carbon (GC) electrode was modified by the electrodeposition of quercetin (QU) on a graphene oxide (GO) film, previously immobilized on the activated glassy carbon surface (aGC). During modification process, QU is oxidized to the corresponding *o*-quinone derivative and adsorbed on the GO/aGC electrode surface following a Michael addition reaction. The GO was characterized using TGA (under air), infrared (FTIR) and Raman spectroscopy. The electrochemical properties of the QU/GO/aGC electrodes were investigated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry and differential pulse voltammetry (DPV). This modified electrode improved the electrochemical response forward the oxidation of noradrenaline (NA), acetaminophen (AC), xanthine (XA) and theophylline (TH), by decreasing the over-potential for the NA and AC electrodes. Under optimal experimental conditions, a good linear relationship between anodic peak current and low concentrations were obtained, achieving LOD of 1.6, 0.39, 0.70 and 0.33  $\mu$ mol L<sup>-1</sup> for NA, AC, XA and TH respectively, Figure 1. The application of the QU/GO/aGC electrode for determination of TH in the presence of high concentrations of NA, AC and XA and drug formulations presented good and reproducible recovery test results.



**Figure 1**. Differential pulse voltammograms obtained into PBS 1 0,1 mol L<sup>-1</sup> pH 7.4 containing NA, AC, XA and TE at QU/GO/aGC electrode (full line), polished GC electrode (dash-dot line) and blank voltammogram (dash line). DPV parameters: modulation time 50 ms, interval time 500 ms, step potential 5 mV and modulation amplitude 50 mV. Concentration of analytes ( $\mu$ mol L<sup>-1</sup>): [NA] = 49.3; [AC] = 20.0; [XA] = 20.0 and [TH] = 38.1.

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# Study of the catalytic efficiency of tantalum oxide supported on Printex 6L carbon for the electrosynthesis of hydrogen peroxide

J.F. Carneiro<sup>a</sup>, J.B. Reis<sup>a</sup>, P. Hammer<sup>b</sup>, M.C. Santos<sup>c</sup>, R. Bertazzoli<sup>d</sup>, M.R.V. Lanza<sup>a</sup>

<sup>a</sup> GPEA – Grupo de Processos Eletroquímicos e Ambientais, IQSC – Instituto de Química de São Carlos,

USP – Universidade de São Paulo, 13560-970 São Carlos, SP, Brasil.

<sup>b</sup> Instituto de Química, UNESP – Universidade do Estado de São Paulo,

14801-970 Araraquara, SP, Brasil

<sup>c</sup> Centro de Ciências Naturais e Humanas, UFABC – Universidade Federal do ABC,

09210-170 Santo André, SP, Brasil

<sup>d</sup> Faculdade de Engenharia Mecânica, UNICAMP – Universidade Estadual de Campinas, 13083-970

Campinas, SP, Brasil

jussarafcarneiro@iqsc.usp.br

In recent years, in situ hydrogen peroxide electrogeneration has become of great interest [1]. Several researchers use this oxidizing agent in advanced oxidation processes (AOPs) [2-3]. However, the relative formation efficiency rates of  $H_2O_2$  can be increased from addition of organic or inorganic modifiers on carbon. In this work, Printex 6L carbon-supported Ta<sub>x</sub>O<sub>y</sub> nanoparticles were prepared by the polymeric precursor method and characterized with X-ray fluorescence (XRF), X-ray diffraction (XRD), transmission electron microscopy (TEM) and and X-ray photoelectron spectroscopy (XPS). The catalysts were prepared in different nominal loading (w/w) relative to the Printex 6L carbon matrix i.e. 0.5; 1.0; 3.0; 5.0; 8.0; 10 and 15 % of the metal. Electrochemical activity of the materials was evaluated towards the oxygen reduction reaction (ORR) using a rotating ring-disk electrode. Electron microscopy images show the high dispersion of  $Ta_2O_5$  nanoparticles on Printex 6L. It was possible to confirm that 5.0 % Ta (w/w) was the best catalyst which shows oxidation current of peroxide ions in the region of mixed control 30.6 % higher than that of Printex 6L. In addition, Ta<sub>2</sub>O<sub>5</sub>/Printex electrodes exhibited overpotential 90-140 mV lower than Printex 6L which implies lower energy consumption for H<sub>2</sub>O<sub>2</sub> electrogeneration. The higher activity for the ORR of the tantalum oxide supports on Printex 6L carbon with respect to carbon black was ascribed essentially to two factors, that is, the transfer of electrons from Ta (V) to  $O_2$  related to redox transition in the region of oxygen reduction and the presence of oxygenated group on carbon modified surface. The enhanced electrocatalytic performance of this electrocatalysts makes them a viable alternative to Gas Diffusion Electrodes for organic wastewater treatment applications. Acknowledgments: CNPq and CAPES for financial support.

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# The catalytic activity of zirconium oxide–Printex 6L carbon composite towards oxygen reduction reaction

J.F. Carneiro<sup>a</sup>, J.B. Reis<sup>a</sup>, P. Hammer<sup>b</sup>, M.C. Santos<sup>c</sup>, R. Bertazzoli<sup>d</sup>, M.R.V. Lanza<sup>a</sup>

<sup>a</sup> GPEA – Grupo de Processos Eletroquímicos e Ambientais, IQSC – Instituto de Química de São Carlos,

USP – Universidade de São Paulo, 13560-970 São Carlos, SP, Brasil.

<sup>b</sup> Instituto de Química, UNESP – Universidade do Estado de São Paulo,

14801-970 Araraquara, SP, Brasil

<sup>c</sup> Centro de Ciências Naturais e Humanas, UFABC – Universidade Federal do ABC,

09210-170 Santo André, SP, Brasil

<sup>d</sup> Faculdade de Engenharia Mecânica, UNICAMP – Universidade Estadual de Campinas, 13083-970

Campinas, SP, Brasil

jussarafcarneiro@iqsc.usp.br

Hydrogen peroxide electrogeneration in the Gas Diffusion Electrode (GDE) are promising since this oxidant is generated at the electrode-solution interface from the oxygen reduction reaction (ORR). However, the relative formation efficiency rates of  $H_2O_2$  can be increased from addition of organic or inorganic modifiers on carbon. In this work, the influence of the content of zirconium oxide on  $H_2O_2$ electrogeneration via the ORR was described. The eletrocatalysts with different nominal loading were prepared by the polymeric precursor method and physically characterized by X-ray fluorescence (XRF). X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The ORR activity of these catalysts was investigated in a 0.1 mol.L<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> (pH = 2) solution and the kinetic parameters were determined by the rotating ring-disk electrode (RRDE) technique. The nanoparticles with average size of 7.7 nm were uniformly loaded on Printex 6L carbon. The XRD patterns and the XPS show only crystalline phase, ZrO<sub>2</sub>, and elevated oxygen concentration on carbon with the presence of the catalyst. It was possible to confirm that 5.0 % Zr (w/w) was the best catalyst which shows  $i_{(H2O2)}$ % equal to 84.2% and  $n_t$  equal to 2.3 electrons vs.  $i_{(H2O2)}$ % equal to 76.5 % and  $n_t$ equal to 2.5 for Printex 6L. Furthermore, the modified electrocatalysts shift the half-wave potential 155 mV for the oxygen reduction to hydrogen peroxide which enables 2-electron ORR at low overpotential. The high catalytic activity observed can be associated with the occurrence of redox transition observed in the cyclic voltammetry. In addition, the ORR can be related to the weak strength of adsorption of oxygen to the metal due to the low center of energy band or a low density of occupied electron states in the electrocatalysts near the Fermi level [1-2]. This adsorption hinders the breaking of the O-O bond resulting in the hydrogen peroxide formation as the final product of the reaction described in Pauling model [3]. The enhanced electrocatalytic performance of this electrocatalysts makes them viable alternative to GDE for organic wastewater treatment application.

Acknowledgments: CNPq and CAPES for financial support.

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# Improvement of Water Splitting Reaction Over Poly(3-hexylthiophene) Modified with Reduced Graphene Oxide

<u>Roger Gonçalves</u>, Fernando C. Moraes and Ernesto Chaves Pereira Federal University of São Carlos (UFSCar) Chemistry Department - Washington Luiz Road, Km 235 - São Carlos - SP - Brazil ernesto@ufscar.br

Solar cells are a promising source for renewable energy, although, at this moment, most of the world's energy consumption still occurs using fossil fuel. From a different point of view, fuel cells have received also considerable attention because they are also a important possibility for energy conversion. In this last case, different fuels can be used, such as small organic molecules and hydrogen. The simplest fuel, of course, is hydrogen. The problem with this compound is its storage, and, depending on its production, the contamination with CO. Then, water electrolysis is a viable reaction to obtain high purity hydrogen, and it is an almost inexhaustible supply of this fuel because the burning hydrogen generates water again. However, the industrial production of hydrogen is a challenge once an increase in the efficiency of reaction and the development of cheap materials as catalyts is needed. Considering this last issue, poly (3-hexylthiophene), P3HT, can be used in the photoelectrochemical water splitting reaction. However, its efficiency to photoconversion is low and the coupling with a second compound has been proposed which reduce the effect of recombination or have a synergistic effect on the generation of photocurrent. In this work, we propose to use reduced graphene oxide (RGO) a modifier to P3HT to enhance its photocatalytical properties towards water splitting. The modified films were deposited over glass covered with indium tin oxide electrodes (ITO). The chemically P3HT has been synthesized by the oxidation of the monomer with FeCl<sub>3</sub> in chloroform at a ratio of 1:4, respectively. The polymerization was carried out for 4 h and the product was washed with methanol, filtered and dried. Graphene oxide has been prepared by Hummer's method. Then, the reduced graphene was obtained by hydrothermal reduction of its oxide. The films were prepared by casting a solution of chloroform containing 2 mg/mL of P3HT + 1 mg/mL of RGO. To compare the results, a second sample was prepared using  $120 \ \mu l$  of 2 mg/mL of P3HT solution with an exposed area of 1 cm<sup>2</sup>. The electrochemical characterization was carried cyclic voltammetry, CV, and Mott-Schottky , M-S, plots in acetonitrile solution containing 0.1 mol L<sup>-1</sup> LiClO<sub>4</sub> and the hydrogen reduction and photocurrents were carried in aqueous KCl 0.1 mol L<sup>-1</sup> under the illumination of a equivalent sun (Xe lamp 250 W). The water splitting reaction curves were obtained by linear potential sweep from 0.7 up to -0.5 V at a v=10 mV s<sup>-1</sup>. From the voltammetric curves, it is possible to observed a change in the oxidation peak characteristic of the polymer, with a displacement for more positive potentials. In addition, there was an increase in peak current and hence in the total anodic charge. From M-S plots it was detected an increase in the number of charge carriers which is 9.8x10<sup>18</sup> for the film without graphene and  $2.4 \times 10^{20}$  to the film with graphene. These results corroborate the improvement observed in water splitting under illumination. There was, however, increased current density under illumination of -42 to -56  $\mu$ A cm<sup>-2</sup> at -0.5 V (vs Ag/AgCl/KCl<sub>3 0M</sub>) and a decrease in the onset potential shifts towards more positive potentials for the RGO+P3HT sample. In summary, it can be concluded that the incorporation of the RGO in P3HT films lead to an improvement in photoelectrochemical properties for the water splitting reaction.

## **Electrochemical Application of Exfoliated Graphite-Diamond Mixed Carbon Electrodes in Water Treatment**

O.A. Arotiba, B. Ntsendwana<sup>1</sup>, M.O. Ama, G. Peleyeju Department of Applied Chemistry, University of Johannesburg, P.O. Box 17011, Doornfontein, 2028, South Africa. oarotiba@uj.ac.za

In the quest for novel electrochemically robust materials for electrochemical application, we present the preparation of a micro-nano mixed carbon electrodes of exfoliated graphite (which exhibits good electro-catalytic property) and diamond (which possesses high oxygen evolution potential) electrodes for the electrochemical degradation of organic pollutants in water. Diamond powder and exfoliated graphite (EG) were mixed in iso-propanol, dried and compressed into EG-diamond pellets and later fabricated into an electrode. The EG-diamond was characterised by electron microscopy, Raman spectroscopy, X-ray diffractometry, X-ray photoelectron spectroscopy and electrochemistry. The results showed a good dispersion of the diamond in the EG and improved potential window. The EG-diamond electrode was employed for the electrochemical oxidation of methylene blue dye. The efficiency of degradation was measured by uv-visible spectroscopy and total organic carbon. The mixed carbon electrode exhibited a higher degradation efficiency than the EG. The kinetics of this electrochemical reaction was studied using the Langmuir Hinshelwood model. The degradation of the dye was also monitored with gas chromatography-mass spectrometry and intermediates were identified. Aside the importance of advance oxidation processes as an alternative or complementary water treatment method, this novel electrode is cheap (diamond dust), easy to prepare and has a robust electrochemistry. We envisage its application in lieu of the more expensive boron doped diamond in the near future.

**Keywords**: exfoliated graphite, diamond, electrochemical degradation, methylene blue, degradation efficiency, water treatment.

# Acid medium evaluation of ORR using catalysts modified with mixed oxides of Niobium and Molybdenum supported on Printex 6L carbon.

L.C. Trevelin<sup>(1,\*)</sup>, R.B. Valim<sup>(1)</sup>, R.S. Rocha<sup>(1)</sup>, M.R.V. Lanza<sup>(1)</sup>

<sup>1</sup> Instituto de Química de São Carlos, Universidade de São Paulo Avenida João Dagnone, nº 1100 - Jardim Santa Angelina. São Carlos – SP – Brasil (CEP 13563-120) \*leandrotrevelin@gmail.com

**Abstract:** The present work aims to study the behavior of the oxygen reduction reaction (ORR) with the mofication of Printex 6L carbon with mixed oxides of Niobium and Molybdenum in a Rotating Ring/Disc Electrode (RRDE). The ORR is a reaction that could proceed by two overall pathways: one uses 4 electrons and generates H<sub>2</sub>O; the second uses 2 electrons to generate H<sub>2</sub>O<sub>2</sub>. Measurements of X-Ray Fluorescence (XRF) (PANanalytical instrument, Rh beam source of 30 eV) were performed for the characterization of the catalysts. The results were expressed in Figure 1a, which can be seen that there is an increase in the characteristic signals of K $\alpha$ , on values of 16.58 KeV and 17.44 KeV for Niobium and Molybdenum respectively, with the increase of the modifier. Linear voltammetry in acid medium (0.1 M K<sub>2</sub>SO<sub>4</sub>) were carried out with the contents of 0.5, 1.0 and 5.0 % of the modifier oxides on (here on named by NbMo) Printex 6L carbon in a potentiostat Autolab 302N, scan rate 5.0 mV s<sup>-1</sup> and RRDE rotation speed of 900 rpm using the porous microlayer technique [1]. For the fixation of the microlayer deposited on RRDE were used 10  $\mu$ L of 0.1% Nafion®. Figure 1b show the results obtained which the only content that shows higher ring current (detection of H<sub>2</sub>O<sub>2</sub> generated) is the 1.0 %.

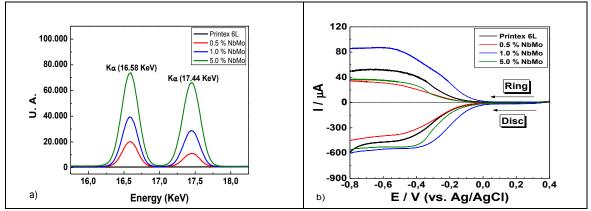


Figure 1: a) Results of XRF experiments b) Results of linear voltammetry experiments.

Using efficiency of hydrogen peroxide equation [2] was obtained an efficiency value of 46.1 % for the Printex 6L carbon coming up to 59.3 % for the catalyst containing 1.0 % of NbMo oxides. Using total number of electrons equation [3] was obtained a value of 3.1 average electrons for the Printex 6L coming up to 2.8 average electrons for the catalyst with 1.0 % of NbMo oxides. Thus, it was concluded that there is a change in the way of ORR occur in presence of the studied catalysts and the content of 1.0 % of the synthetized oxides supported on printex 6L has the capability of enhance the 2 electrons pathway of ORR leading to a higher production of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

## Acknowledgments:

Fapesp e Capes

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# The effect of diamond/graphite carbon compositions in electrochemical oxidation reactivity

<u>Fernanda Souza<sup>1</sup></u>, Marcos Lanza<sup>1</sup>, Cristina Saez<sup>2</sup>, Pablo Canizares<sup>2</sup>, Manuel Rodrigo<sup>2</sup> <sup>1</sup>Chemical and Molecular Physical Department. Institute of Chemistry of Sao Carlos, University of Sao Paulo. Av. Trabalhador Sao Carlense 760 Sao Carlos. SP. Brazil. <sup>2</sup>Chemical Engineering Department. Faculty of Chemical Sciences and Technologies, University of Castilla-La Mancha. Av. Camilo José Cela 12.13005 Ciudad Real. Spain fersouza.usp@gmail.com

In recent years, a large number of publications have demonstrated the efficiency of the electrochemical process with diamond anodes for the destruction of bio-refractory organic pollutants<sup>1</sup>. These materials exhibit excellent properties such as higher chemical and electrochemical stability, robustness, weak electrode fouling and long service life. However, little attention is paid to role of the  $sp^3:sp^2$  carbon ratio, which may affect the efficiency of electrochemical process significantly. Previews works demonstrated that high graphite content favors direct oxidation of the pollutant on the electro de surface and it leads to the formation of many intermediates. Conversely, high diamond content seems to favor the complete oxidation of the organic to CO<sub>2</sub>, thanks to the contribution of the oxidants (hydroxyl radicals and electro generated reagents) present in a region close to the electrode surface<sup>2</sup>. This work aims to assess of the effect of increasing the sp<sup>3</sup>:sp<sup>2</sup> ratio on the results of the treatment of a synthetic wastewater containing pesticides and chlorides. The herbicide 2,4- dichlorophenoxyacetic acid (2,4-D) was chosen as compound model since 2, 4 D is a extensively used in agriculture in many commercial products and it has a high solubility in water. The electrolyses were conducted in a DiaCell<sup>®</sup> type 101 supplied by Adamant Technologies. Boron-doped diamond electrodes (p-Si-BDD) were used as anode and cathode, respectively. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm<sup>2</sup>. The BDD coating have a with a film thickness of 2mm and resistivity of 100 m $\Omega$ .cm. Boron concentration was 500 ppm and the relation sp<sup>3</sup>/sp<sup>2</sup> range from 165 to 323. Results obtained showed that complete mineralization was attained in tests carried out with all sp<sup>3</sup>-sp<sup>2</sup> ratios tested and that the mineralization process during electrolysis of 2,4-D fits well to a first order kinetic (explained by the diffusion control of the rate of the electrochemical process due to the low concentration of pollutants and by effect of mediated oxidation). The higher the sp<sup>3</sup>:sp<sup>2</sup> ratio in the anode, the more efficient and faster is the depletion of 2,4-D and its conversion into carbon dioxide with an almost negligible formation of intermediates, pointing out the significance of this parameter on mineralization. The observation confirms that the anodes with higher diamond content favors the electrochemical combustion pathway while the anodes with higher graphite content favors the conversion of the pollutant to intermediates, even in wastewater with low concentration of pollutant in which mediated processes could play an important role. Moreover, results clearly demonstrate that other important processes, such as the oxidation of chlorides, are also affected by the sp<sup>3</sup>:sp<sup>2</sup> ratio and the production of hazardous species such as chlorates and perchlorates can be minimized by a proper choice of the  $sp^3:sp^2$  ratio of anodes.

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# Electrochemical Properties of the Oxo-manganese-*Schiff* Complex and its Electrocatalytic Application as Enzymatic Biomimicking

Wesley B. S. Machini and Marcos F. S. Teixeira

São Paulo State University (UNESP), Faculty of Science and Technology, Department of Physics, Chemistry and Biology, Presidente Prudente/SP – Brazil. \*funcao@fct.unesp.br

Many different oxo-manganese-Schiff complexes with biomimetic properties, such as involvement in photosystem II, have been applied to bioinorganic and catalysis [1]. Furthermore, these complexes have received significant contributions by presenting interesting electrochemical properties. Initially, the electrochemical properties was studied by cyclic voltammetry (CV) using a glassy carbon (GC) electrode as working electrode in CH<sub>2</sub>Cl<sub>2</sub>/0.1 mol L<sup>-1</sup> TBAP containing 1.0 mmol L<sup>-1</sup> of  $[Mn^{IV}(\mu-O)(salpn)]_2$ complex under a N<sub>2(g)</sub> atmosphere. The cyclic voltammogram exhibits one redox couple, being the  $E_{pa}$  at -390 mV and  $E_{pc}$  at -517 mV vs. SCE, that correspond to the Mn<sup>IV</sup>/Mn<sup>III</sup> redox process. A variation of potential ( $\Delta E_p$ ) equivalent to 127 mV vs. SCE and a half potential ( $E_{p/2}$ ) of -454 mV vs. SCE, indicating a quasi-reversible process, were obtained. The scan rate study in organic solution showed different behaviors for low (5 mV s<sup>-1</sup> at 50 mV s<sup>-1</sup>) and high (75 to 200 mV s<sup>-1</sup>) values. This fact can be explained by the quasi-reversible system of the  $[Mn^{IV}(\mu-O)(salpn)]_2$  complex in solution, which the reaction kinetics of oxidation and reduction are considered simultaneously and the extent of irreversibility of the system increases with increasing scan rate, along with a decrease in current peak on the reversible case and increasing separation between anodic and cathodic peaks. Analysing the relationship between log  $I_{pa}$ vs.  $\log v$  is evident that the electronic transfer behavior of the complex in solution is adsorptivediffusional mixed type, wherein the adsorptive process is noted for rates up to 50 mV s<sup>-1</sup> ( $\theta_{exp} = 1.05$ ;  $\theta_{theor}$ = 1.00), authenticating the electron transfer control is a surface mechanism (adsorptive process), while a diffusional process is denoted for equal and higher rates to 75 mV s<sup>-1</sup> ( $\theta_{exp} = 0.62$ ;  $\theta_{theor} = 0.50$ ). The electrochemical behavior in solution was also analysed by differential pulse voltammetry (DPV), applying a potential range of -0.8 V to 0.0 V vs. ECS (oxidation and reduction) at 25 mV s<sup>-1</sup> with 50 mV pulse. Through these voltammograms, two redox processes in the anodic and cathodic direction were observed, which were different results from those obtained using the technique of cyclic voltammetry. The appearance of peaks at -487 mV and -236 mV vs. SCE in the anodic direction and -488 mV and -163 mV vs. SCE in the cathodic direction reveals an effect of comproportionation, due to oxidation/reduction of one metal center resulted of a change in electronic density, which it is readily communicated to the other metal center through the oxo-bridge, making it more difficult a second step of oxidation/reduction [3]. In this way, this effect was evaluated through the calculation of comproportionation constant  $(K_c)$  and Gibbs energy ( $\Delta G^{\circ}$ ) [4]. Independent of the scan rate applied, the [Mn<sup>IV</sup>( $\mu$ -O)(*salpn*)]<sub>2</sub> complex can be classified as a compound of very weak electronic interaction between the redox centers (*Class I*), due to their  $K_C$  in scale of 10<sup>-6</sup>. According to the  $\Delta G^{\circ}$  obtained, the complex in solution presented a system thermodynamically unfavorable. The investigation of electrocatalytic activity of the  $[Mn^{IV}(\mu-O)(salpn)]_2$ as enzymatic biomimicking in the reduction of hydrogen peroxide was realized in the same conditions. The cyclic voltammograms obtained to the  $[Mn^{IV}(\mu-O)(salpn)]_2$  complex in absence and presence of 1.00  $\mu$ mol L<sup>-1</sup>, 2.50  $\mu$ mol L<sup>-1</sup> e 5.00  $\mu$ mol L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> showed an increase of peak current with an increase of H<sub>2</sub>O<sub>2</sub> concentration. Differently was observed with GC electrode in the absence of the complex, since it was not possible the direct detection of H<sub>2</sub>O<sub>2</sub>. The electrocatalytic mechanism of H<sub>2</sub>O<sub>2</sub> reduction by  $[Mn^{IV}(\mu-O)(salpn)]_2$  complex involves two stages of reduction/oxidation with two electrons [5], similarly to the catalytic cycle of the catalase enzyme, proving the biomimetic properties. Finally, the determination of H<sub>2</sub>O<sub>2</sub> was assessed using the technique of linear sweep voltammetry for adding standards of the analyte (1.0 mmol L<sup>-1</sup>) to the solution containing the  $[Mn^{IV}(\mu-O)(salpn)]_2$  complex. The increase of cathodic peak current on the basis of successive additions was recorded in order to evaluate the evolution of catalytic reduction of  $H_2O_2$  in the complex. Thus, the peak current values were linear in a concentration range from 0.5  $\mu$ mol L<sup>-1</sup> to 5.5  $\mu$ mol L<sup>-1</sup>, with a quantification of 1.26  $\times$  10<sup>-4</sup> mol L<sup>-1</sup> and detection limit of  $3.78 \times 10^{-5}$  mol L<sup>-1</sup> with a sensitivity of 0.66  $\mu$ A L mol<sup>-1</sup>.

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## Towards Rational Design of Gold Platforms for Protein Biosensing with Various Graphene-Derived Materials

Emiliano N. Primo<sup>1</sup>, M. Dolores Rubianes<sup>1</sup>, Gustavo A. Rivas<sup>1</sup>, Soledad Bollo<sup>2,3</sup>\*

<sup>1</sup>INFIQC (UNC-CONICET), Departamento de Fisicoquímica, Facultad de Ciencias Químicas,

Universidad Nacional de Córdoba, X5000GYA Córdoba, Argentina.

<sup>2</sup> Laboratorio de Bioelectroquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, 8380492, Santiago, Chile. <sup>3</sup>Advanced Center for Chronic Diseases (ACCDiS). Universidad de

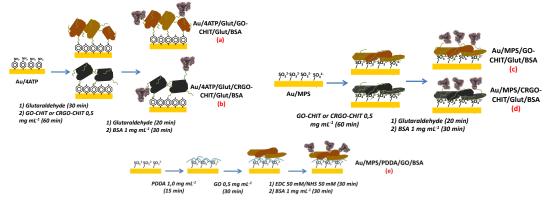
*Chile.* \**sbollo*@*ciq.uchile.cl* 

Graphene and its precursor in the chemical route synthesis, the graphene oxide (GO), are excellent candidates for electrochemical biosensing applications, due to its conductivity properties, good biocompatibility and various functionalization possibilities. The crucial development of GO-related electrochemical applications lies in the design of simple and reliable assembly routes for the preparation and functionalization of Gr and GO-based electrodes. Fine control over assembly conditions is responsible for the range of novel properties exhibited by these kinds of sensing platforms.

Following the above stated issues, we proposed to study how the immobilization strategies used to attach GO and GO functionalized with chitosan (CHIT) to Au electrodes affect the electrochemical/interfacial properties and protein loading of the resulting platforms. For this purpose, commercially available GO was used. The functionalization of GO with CHIT was performed with the aid of EDC/NHS coupling agents and the reduction of GO-CHIT was performed with NaBH<sub>4</sub> and further confirmed through IR and Raman Spectroscopies and H<sup>1</sup>-NMR. The immobilization strategies were:

a. <u>through covalent assembly</u>: by using glutaraldehyde as linking agent, Au electrodes modified with 4aminothiophenol (4ATP) were modified with GO-CHIT (Scheme **a**) and CRGO-CHIT (Scheme **b**).

b. <u>through non-covalent assembly</u>: by means of layer-by-layer self-assembly, mediated through electrostatic interactions. GO-CHIT and CRGO-CHIT were assembled over Au modified with 3-mercapto-1-propanesulfonate (MPS)(Scheme c and d, respectively). For the assembling of GO, a previous layer of a polycation (PDDA) was deposited over Au/MPS (Scheme e).



In all cases, covalent linking of BSA was performed after immobilization of GO as a model protein.

The voltamperometric and impedance response of redox markers ferricyanide,  $H_2O_2$  and hydroquinone provided the electrochemical information in each step of the platform modification. Oxidation current of  $H_2O_2$  and hydroquinone decreased after the GO-CHIT and CRGO-CHIT covalent immobilization while in the case of non-covalent assembly strategies, it increased. These results, combined with SEM and surface plasmon resonance (SPR) measures over Au disks, showed that the covalent strategy provided the lowest degree of grapheneous material loading over the Au modified surface.

Scanning electrochemical microscopy (using ferrocenemethanol as redox mediator) also provided evidence of different kinds of local conductivity of Au/MPS/PDDA/GO, Au/MPS/GO-CHIT and Au/MPS/CRGO-CHIT platforms, being the latter the one that has the best conductivity due to restoration of the sp<sup>2</sup> graphene network.

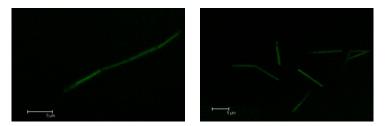
The different spatial arrangements of GO and CRGO in covalent and non-covalent strategies also strongly influence the sensibility of the Au modified platform to the blocking of the surface when BSA was linked. This step is critical taking into account that the platform is going to be used to attach an antibody for the development of an electrochemical immunosensor.

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## Streptavidin-Functionalized Ferromagnetic Nickel Nanowires: a New Tool for Bioanalytical Applications

<u>P. Fanjul-Bolado</u><sup>\*</sup>, M.M.P.S. Neves, D. Hernández-Santos DropSens, S.L., Edificio CEEI, Parque Tecnológico de Asturias, 33428 Llanera, Asturias, Spain <sup>\*</sup>(pfanjul@dropsens.com)

Nowadays, the advances in nanotechnology opened new opportunities to explore modern analytical applications. Among them, metal-based nanowires are attracting great attention as building blocks for sensing devices in chemistry and biochemistry [1]. Therefore, DropSens S.L. (www.dropsens.com) developed nickel nanowires bio-functionalized with streptavidin (DRP-NINW-STR). This innovative and highly-stable streptavidin functionalized nanomaterial is an excellent option for the immobilization of a large amount of biotinylated molecules. Moreover, due to nickel ferromagnetic behaviour [2] this new product is a perfect candidate to be use in magnet-based (bio)assays. The efficient immobilization of biotinylated molecules was successfully demonstrated and this new DRP-NINW-STR was effectively applied in the detection of a 22-mer oligonucleotide. This functionalized nanomaterial was also characterized by confocal and transmission electron microscopy. The efficient coating of nickel nanowires with streptavidin as well as the excellent control of DRP-NINW-STR by applying a magnetic external field was verified. These nanowires modified with streptavidin appear as an exciting nanomaterial that can be applied within a wide range of fields, such as chemistry and electrochemistry, biochemistry, immunology, cell and molecular biology.



**Figure 1.** Confocal microscopy images of DRP-NINW-STR modified with an oligonucleotide labelled with biotin at 3'end and fluorescein at 5'end.

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### Acknowledgments

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# Preparation, Characterization and Application of a Novel Composite Obtained Through Zr(IV) Isopropoxide and Phosphoric Acid

T. F. S da Silveira<sup>1</sup> and D. R do Carmo<sup>1</sup>

<sup>1</sup>Faculdade de Engenharia de Ilha Solteira, Universidade Estadual Paulista "Júlio de Mesquita Filho", Departamento de Física e Química. Av. Brasil, 56, CEP 15385-000, Ilha Solteira, SP, Brazil.

tay lafser anton i @gmail.com

Composite materials are composed of two or more distinct phases in order to achieve a combination of properties that are not exhibited by any single material, and also to incorporate the best characteristics of each component material phases. Inorganic composites are those in which the matrix is a metallic or ceramic material [1].

In this work we report the preparation and characterization of composite Zirconia Phosphated (ZrP) from aqueous phosphoric acid and Zirconium (IV) Isopropoxide Isopropanol Complex. Techniques such as, Fourier Transform Infrared Spectroscopy (FTIR), <sup>31</sup>P and <sup>13</sup>C Nuclear Magnetic Resonance (NMR), Energy Dispersive X-ray Spectroscopy (EDS) and Thermogravimetric Analysis (TG) were used for characterization of this composite.

Vibrational spectrum for ZrP, it was observed a broad band in the region of 3700 to 3000 cm<sup>-1</sup> which was attributed to symmetrical and asymmetrical –OH stretching, there is also a narrow band in 1632 cm<sup>-1</sup> that was assigned to H–O–H bond of water and a strong absorption at 1010 cm<sup>-1</sup> which was attributed to  $\Box$  (P=O) stretching [2,3]. The bands presented in the region of 580 to 400 cm<sup>-1</sup> correspond to bonds Zr-O [4].

The results obtained by energy dispersive X-ray spectroscopy confirmed the presence of Zr, P and O in the formed composite, and any C has been detected in concordance of NMR of <sup>13</sup>C in solid state, this is an indicative of preparation was conducted with success. The solid-state <sup>31</sup>P NMR spectrum of ZrP showed main peak at -18.77 ppm and a weaker peak at -12.20 ppm. A shoulder with very weak intensity is also observed at about -23.82 ppm.

The TG curves of ZrP showed three steps. First step occurs in the range  $25-130^{\circ}$ C (10,5%) and can be attributed to the loss of adsorbed water, while second step can be attributed to the loss of water due to the condensation of the HPO<sub>4</sub> groups and occurs in the range  $130-480^{\circ}$ C (7%). It was observed a third step at temperatures above  $480^{\circ}$ C, which there was no w eight loss and the residue can be attributed to the formation of zirconium pyrophosphated [5].

As an application of new material, ZrP was reacted with silver ions (ZrPAg) and subsequent addition of potassium hexacyanoferrate (III) (ZrPAgH). The electrochemical behaviour of the composite (ZrPAgH) was verified by cyclic voltammetry using of a graphite paste electrode in a potential range of 0.2 to 0.9 V (*vs* Ag/AgCl). The modified graphite paste electrode could be used in the electrocatalytic oxidation of N-acetylcysteine in a linear range from  $8.0 \times 10^{-6}$  to  $9.0 \times 10^{-5}$  mol L<sup>-1</sup> with a limit detection of  $7.42 \times 10^{-6}$  mol L<sup>-1</sup> and relative standard deviation of  $\pm 5\%$  (n = 3) and amperometric sensitivity 2.40 mA mol L<sup>-1</sup>.

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# Effect of reduction method of graphene oxide on the electrochemical response of a DNA biosensor

Soledad Bollo<sup>1</sup>, Daniela Báez<sup>1</sup>, Claudia Yañez<sup>1</sup>, José F. Marco<sup>2</sup>, Helena Pardo<sup>3</sup>, Ignacio Laborda<sup>3</sup> <sup>1</sup> Laboratorio de Bioelectroquímica, Facultad de Ciencias Químicas y Farmacéuticas, U. de Chile, Sergio Livingstone Polhammer 1007, Independencia, Santiago, Chile <sup>2</sup> Instituto de Química Física Rocasolano. CSIC, Madrid-España. <sup>3</sup> Facultad de Química, U. de la República de Uruguay, Montevideo-Uruguay. sbollo@ciq.uchile.cl

The use of graphene derivatives like reduced graphene oxide (RGO) are being highly used in the development of DNA biosensors due to their facile fabrication, high sensitivity and biocompatible nature. These nanomaterials have improved the electrochemical response which could be attributed to the presence of more  $sp^2$  like planes and edge defects in graphene when is compared with other carbon nanostructures like carbon nanotubes. On the other hand the method of reduction could alter the electrochemical response.

In this work we compare a glassy carbon electrode modified with four kinds of reduced graphene oxides (RGO) on the electrochemical response when a single strand of DNA has been immobilized. RGOs were made from the reduction of graphene oxide using: hydrothermal (hT-RGO), chemical (C-RGO), thermal (T-RGO) and electrochemical (E-RGO) methods of reduction. All RGOs were dispersed in a chitosan-water (3:1) mixture. The ss-DNA immobilization was achieved through immersion of the modified electrode in a stirred solution containing ss-DNA. The adsorption of ss-DNA was evaluated through the oxidation of guanine measured by differential pulse voltammetry (DVP).

Raman and X-ray photoelectron spectroscopic characterization (table) show an inverse correlation between the amount of oxygen in the samples and the degree of graphitic defects. These results are also related with the higher capacitive currents obtained using thermal and electrochemical reduced materials than C-RGO and hT-RGO.

All RGOs were used to evaluate the electrochemical behavior of ss-DNA. Table shows the obtained peak current values after 10 min of accumulation time of 15  $\mu$ M of ss-DNA. Clearly the higher values were obtained using T-RGO and E-RGO. Also a decrease in the peak potential value was observed for T-RGO (0.896 V) while for the other RGO the peak potential was closer to 0.945 V.

In conclusion, the reduction method that introduces larger defects and less oxygen function improves electroanalytical response.

Table: Ratio of the intensities D and G Raman bands, oxygen 1s and carbon 1s taken from the XPS spectra and capacitive current taken from cyclic voltametry at 0.23 V.

RGO	Raman	XPS	CV	ss-DNA
	$I_D/I_G$	O/C	i (µA) at 0.23 V	oxidation current
CRGO	2.39	0.28	4.80	0.37
hTRGO	2.37	0.19	8.69	0.36
TRGO	2.71	0.17	39.0	0.66
ERGO	2.83	0.15	35.9	0.59

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#### Silsesquioxane Organofunctionalized with Pamam Dendrimer and Subsequent Reaction With Copper and Potassium Hexacyanoferrate (III) for Determination of Ascorbic Acid

D. R. Silvestrini<sup>1</sup>, U. O. Bicalho<sup>1</sup> and D. R do Carmo<sup>1</sup>

<sup>1</sup>Faculdade de Engenharia de Ilha Solteira, Universidade Estadual Paulista "Júlio de Mesquita Filho", Departamento de Física e Química. Av. Brasil, 56, CEP 15385-000, Ilha Solteira, SP, Brazil.

daniela\_silvestrini@me.com

Silsesquioxanes or spherosiloxanes are nanostructured materials wich have the empirical formula  $(\text{RsiO}_{1.5})_n$ , where R can be a hydrogen or any organic group and *n* is an integer number that can vary, in n  $\geq 4$  [1]. Dendrimers are synthetic, spherical, mono-disperse macromolecules of nanometer dimentions, prepared by the iterative synthetic methodology. PAMAM dendrimers are biocompatable, water-soluble and posses terminal modifiable amine functional groups for binding various targeting or guest molecules. The internal cavities of PAMAM dendrimers posses host or guest metals, molecules because of the unique functional architecture, which contains tertiary amines and amide linkages [2].

This work presents a studies of a novel composite formed by interaction of a octa(3chloropropyl)octasilsesquioxane [3] modified with PAMAM G. 0 dendrimer and its subsequent reaction with copper and potassium hexacyanoferrate (III) (CuHSP). Techniques such as, Fourier Transform Infrared Spectroscopy (FTIR), <sup>29</sup>Si and <sup>13</sup>C Nuclear Magnetic Resonance (NMR), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Thermogravimetric Analysis (TGA) and Electrochemical Techniques were used for characterization of this novel composite.

The electrochemical behavior of the composite was verified by cyclic voltammetry using a graphite paste electrode modified with CuHSP in a potential range of 0.20 to 0.95 V (vs  $Ag/AgCl_{(sat.)}$ ). The modified graphite paste electrode could be used in the electrocatalytic oxidation of Ascorbic Acid.

The cyclic voltammogram of the modified graphite paste electrode with CuHSP (20% w/w), showed two redox couples with formal potential  $E^{0'}_{1} = 0.26$  and  $E^{0'}_{II} = 0.72$  V (vs Ag/AgCl<sub>(sat.)</sub>, KCl, 1.0 mol L<sup>-1</sup>, v = 20 mV s<sup>-1</sup>), attibuted to Cu<sup>1</sup>/Cu<sup>II</sup> and Fe<sup>II</sup>(CN)<sub>6</sub>/Fe<sup>III</sup>(CN)<sub>6</sub> [4], respectively. The modified electrode showed a linear response from  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> with the corresponding equation Y(A) =  $6.343 \times 10^{-6} + 0.019$  [Ascorbic Acid], and a correlation coefficient of r<sup>2</sup> = 0.999. The method showed a detection limit of  $2.737 \times 10^{-5}$  mol L<sup>-1</sup> with a relative standard deviation of ±4% (n = 3) and amperometric sensitivity of 0.019 A mol L<sup>-1</sup>.

The CuHSP system was also characterized by Chronoamperometry. The chronoamperometry for this system (CuHSP, 20% w/w), showed a linear response from  $5.0 \times 10^{-6}$  to  $4.0 \times 10^{-5}$  mol L<sup>-1</sup> with the corresponding equation Y( $\mu$ A) = 2.729 + 455921.420 [Ascorbic Acid], and a correlation coefficient of  $r^2$  = 0.999. The method showed a detection limit of  $1.66 \times 10^{-6}$  mol L<sup>-1</sup> and amperometric sensitivity of 0.455 A mol L<sup>-1</sup>.

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# Removal of Textile Dye RB-19 Using a Filter-Press Reactor with Reticulated Vitreous Carbon as Cathode

Vanessa M. Vasconcelos<sup>a\*</sup>, Marcos R. V. Lanza<sup>a</sup>, Carlos Ponce-de-Leon<sup>b</sup>

<sup>a</sup>University of Sao Paulo - Institute of Chemistry of Sao Carlos – 13566-590 - Sao Carlos – SP- Brazil <sup>b</sup>University of Southampton – Faculty of Engineering and the Environment – SO17 1BJ – Southampton -England

\*vanessavasconcelos@iqsc.usp.br

Wastewater from the textile industry is considered one of the most problematic effluents mainly because they contain organic dyes such as Reactive Blue 19 (RB-19) which is resistant to degradation and has a half-life of up to 46 years at pH 7 and 25 °C [1]. Due to its high solubility in water, RB-19 dye can stay in the environment for a long time if it is discharged without adequate treatment. Therefore, the main purpose of this study was to degrade Reactive Blue 19 dye via Advanced Oxidation Processes (AOP) using Reticulated Vitreous Carbon (RVC) working electrode as cathode for the reduction of oxygen to generate hydrogen peroxide. The electrode was fitted in a filter-press flow cell together with a borondoped diamond electrode as counter electrode, in two separated compartments [2] separated by a Nafion membrane. The potential of the RVC electrode was monitored by an Ag/AgCl reference electrode in saturated KCl solution. The electrolyte (0.60 L) was an aqueous solution containing 25 mg L<sup>-1</sup> of RB-19 dye in 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, at pH 3 adjusted with H<sub>2</sub>SO<sub>4</sub>. The electrolysis were carried out by applying constant potential of -0.4 V vs. Ag/AgCl and using different concentration of Fe<sup>2+</sup> (0, 0.01, 0.05 and 0.1 mM) to generate the Fenton reactant <sup>•</sup>OH. In order to evaluate the efficiency of the degradation process, samples were collected at selected times and analysed using a UV-Visible (UV/VIS) Spectrophotometry (200-800 nm) and a TOC-VCPN analyser. The efficiency of degradation improved with the concentration of  $Fe^{2+}$  ions and time of electrolysis. Without  $Fe^{2+}$  in solution, 32% color removal was achieved after 90 min of electrolysis whereas using 0.01 mM of  $Fe^{2+}$  the color removal achieved 54%. When 0.05 and 0.1 mM of Fe<sup>2+</sup> were used, more than 94% in color removal was achieved in 60 and 30 minutes respectively showing how the kinetic of the degradation reaction improved with the concentration of  $Fe^{2+}$  ions. This finding agree with Siddique et al. [3] that found less than 10% of color removal using only  $H_2O_2$ however, when they carried out the Fenton reaction more than 50% of color removal was observed for a solution containing RB-19 dye. TOC removal also improved when the concentration of Fe<sup>2+</sup> increased. The highest TOC removal was 60% using 0.01 mM of Fe<sup>2+</sup> after 90 min of electrolysis. In this condition, the total dye removal was achieved in 30 min however other organic products such as carboxylic acid were formed during the electrolysis since total mineralization was not observed. The findings show that total color removal, i.e., rupture of the chromophore groups, is easier than total mineralization since using 0.01 mM of Fe<sup>2+</sup> total removal of RB-19 dye was achieved in 30 min of electrolysis whereas only 60% of TOC removal was measured after 90 min of electrolysis. Less energy consumption (0.14 kWh g<sup>-1</sup>) was achieved when 0.05 mM of  $Fe^{2+}$  was used; in this condition, 50% of TOC was removed. Energy consumption using 0.01 and 0.1 mM of  $Fe^{2+}$  were 0.36 and 0.20 kWh g<sup>-1</sup>, respectively. Reticulated Vitreous Carbon showed to be a promising material to be used in the treatment of colorful solution since it was able to remove completely the RB-19 color from the solution as well to promote partial mineralization.

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#### **Electrochemical Impedance Spectroscopic Study of Poly(Bismarck R)**

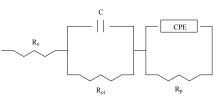
Marcos F. S. Teixeira<sup>1</sup>, Wesley B. S. Machini<sup>1</sup>, Diego N. David-Parra<sup>1</sup>, Carla Gouveia-Caridade<sup>2</sup>, Christopher M. Brett<sup>2</sup> <sup>1</sup>Faculty of Science and Technology, São Paulo State University (UNESP), Brazil <sup>2</sup>Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal

funcao@fct.unesp.br

Among the different polymers found in the literature, the polymeric film of poly(Bismarck R) appear to be attractive candidate for electrochemical studies due to the satisfactory stability in different aqueous electrolytes. Electrochemical impedance spectroscopy (EIS) is valuable technique for determining the properties of poly(Bismarck R) and the analysis of data affords information on charge transfer resistance and specific capacitances.

In this work, the polymer growth of Bismarck R was obtained by CV method at a scan rate of 100 mV s<sup>-1</sup>, applying 100 scans on carbon and on fluorine tin oxide electrodes in solution containing 10 mmol/L Bismarck R and 1.0 mol/L HCl. Electrochemical impedance measurements were done with a PC-controlled Solartron coupled to a Solartron 1286 electrochemical interface using ZPlot 2.4 software. A sinusoidal voltage perturbation of amplitude 10 mV rms was applied in the frequency range between 65 kHz and 0.1 Hz with 10 frequency steps per decade. EIS measurements were performed in 10 mmol/L HCL solution containing 0.5 mol/L KCl.

Complex-plane plots were obtained at -0.35 V and 0.30 V for the electrode coated poly(Bismarck R). The spectrum (Nyquist plot) obtained for the reduced state of poly(Bismarck R) is formed by two typical regions. The first region consists of a small semicircle at high frequencies (100 Hz - 6500 Hz) followed by a straight line with a slope slightly below  $\pi/4$ . The charge transfer resistance (28.2  $\Omega/\text{cm}^2$ ) value can be associated with the redox processes of the azo group within the polymeric film. The second region of a bigger semicircle expanding over the middle and low-frequency range is related to the ion charge transfer at the substrate/aqueous solution interface. An equivalent circuit of three components is proposed:



The CPE component is a constant phase element due the interfacial irregularities. On the other hand, the spectrum obtained for the oxidized state of poly(Bismarck R) show be a conductor material which indicates the decrease of the electron transfer resistance at the electrode/ electrolyte interface. Other studies with different thicknesses of the polymer film have been studied to better understand the system.

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#### Synthesis and characterization of nickel (II) hydroxide particles on Silica/GO matrix and its application in a sensitive electrochemical sensor for vitamin D determination.

Thiago C. Canevari, Fernando H., Cincotto, Sergio A. S. Machado

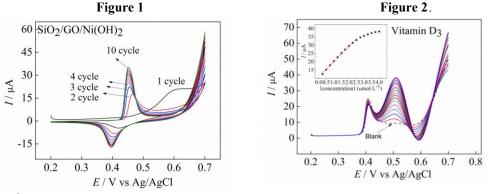
Institute of Chemistry, State University of São Paulo, PO Box 780, 13560-970 São Carlos, SP, Brazil; sasmach@iqsc.usp.br

Hybrid organic-inorganic materials based on silica-containing carbon allotropes have long been used as a basis to support the development of electrochemical sensors, due to their high chemical stability, robustness, functional groups presence and excellent electrochemical properties<sup>1</sup>.

Graphene is currently the most widely used carbon allotrope in the development of hybrid materials. It consists of a single atomic carbon sheet and exist in the oxidized (GO) and reduced (GR) forms, which differ in the amount of functional groups, number and types of defects and consequently its properties. Due to its excellent conductive properties and functional groups, it has been largely used in the synthesis of quite suitable new materials for the development of electrochemical sensors <sup>2,3</sup>.

Ni(OH)<sub>2</sub> is a polymorphic material that exists in  $\alpha$ ,  $\beta$  and  $\gamma$  phases as main structures. The  $\gamma$  phase is represented by NiOOH species that can be obtained as the result of electrochemical oxidation of  $\alpha$  and  $\beta$  species in alkaline medium and is one of the most electrochemically active oxidized Ni compounds<sup>4</sup>.

The electrochemical behavior of the hybrid material SiO<sub>2</sub>/GO/Ni(OH)<sub>2</sub>/GCE was initially studied by cyclic voltammetry in 0.1 mol  $L^{-1}$  NaOH, pH = 13. The results are presented in Figure 1, in which the first cycle (black line) presents a large oxidation plateau, beginning at approximately 0.55 V, followed by a quite small reduction peak around +0.42 V. This voltammetric profile is attributed to the response of  $\alpha$ -Ni(OH)<sub>2</sub> species . After the second cycle, the voltammetric response changes, exhibiting a much more reversible profile which can then be associated with the transformation of  $\beta$ -Ni(OH)2 into  $\alpha$ -Ni(OH)<sub>2</sub>. This transformation is thermodynamically favorable and is characterized by an increase in the reversibility of the redox peaks. Therefore, after the 2nd cycle, a shift in the potential of the redox couple is observed towards less positive values (around  $E_{OX}$ = + 0.465 V and  $\dot{E}_{Red}$ = + 0.405 V), which is attributed to the formation and reduction of the corresponding Ni(OOH) phase. From the 5-cycle, the redox potential values stabilize around  $E_{OX}$  = + 0.45 V and  $E_{Red}$  = + 0.39 V. The Ni<sup>2+</sup> and Ni<sup>3+</sup> species represent, respectively, the reversible transformation of type  $\alpha$ -Ni(OH)<sub>2</sub> to  $\gamma$ -NiOOH in alkaline medium. Figure 2 shows the determination of Vitamin D<sub>3</sub> using the SiO<sub>2</sub>/GO/Ni(OH)<sub>2</sub>/GCE electrode in NaOH solution, pH 13. It can be seen that the oxidation peak currents increased proportionally to the Vitamin D<sub>3</sub> concentration in the range from 2.5 x 10<sup>-7</sup> to 4.25 x 10<sup>-6</sup> mol L<sup>-1</sup>, indicating that the modified electrode presents excellent electrocatalytic response in potential around 0.5 V and thus can be used for the determination of Vitamin D<sub>3</sub> in real samples<sup>5</sup>. The limit of detection (LOD) of vitamin D3 was calculated using statistical methods to be  $3.26 \times 10^{-9}$  mol L<sup>-1</sup>, which corresponds to  $1.25 \mu g$  of vitamin D<sub>3</sub>.



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# Simultaneous determination of epinephrine and dopamine by electrochemical reduction on the hybrid material SiO<sub>2</sub>/graphene content Ag nanoparticles.

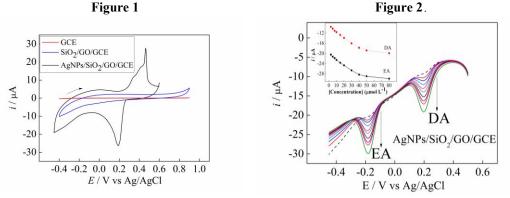
Sergio A. S. Machado, Fernando H. Cincotto, Thiago C. Canevari, Anderson M. Campos, Institute of Chemistry, State University of São Paulo, PO Box 780, 13560-970 São Carlos, SP, Brazil; sasmach@iqsc.usp.br

Hybrid materials based on mesoporous silica / carbon combination have attracted the attention of many researchers due to the possibility of combining the main features that silica and carbon-based materials may present in a single material. Graphene consists of a single sheet of graphite containing carbon atoms linked together by pi ( $\pi$ ) linkages contributing to the formation of a delocalized electron network. Graphene has a single atomic plane and present excellent conductivity, high surface area, high elasticity, adjustable band-gap, biocompatibility, robustness and, especially, endless possibilities for modification or functionalization of its carbon chain, making it an excellent substrate for the development of electrochemical sensors<sup>1-2</sup>.

Mesoporous silica is presently widely used as a substrate for the development of electrochemical sensors due to its characteristic pores with diameters between 2 and 50 nanometers, chemical resistance and thermal, and high surface area. Thus, the process of mass transfer is favored by its mesoporous structure, providing electrochemical sensors with high sensitivity and low limits of detection.<sup>3</sup>

Silver nanoparticles (AgNPs) have been widely used in the development of electrochemical sensors due their biocompatibility and excellent conductive properties, improving the sensitivity of (bio)electrochemical sensors with respect to analytes studied <sup>4</sup>.

Figure 1 shows cyclic voltammograms (CV) profiles at the bare glassy carbon (GCE), SiO2/GO/GCE and AgNPs/SiO2/GO/GCE in PBS 7.0 with a scan rate of 20 mV s-1. As can be been, the modified electrode of the AgNPs/SiO<sub>2</sub>/GO hybrid material, presented two redox peaks differently of the modified SiO<sub>2</sub>/GO hybrid material electrode and bare GCE. The peaks with potentials  $E_{OX1}$ = + 0.45 V and  $E_{Red1}$ = + 0.2 V were related to the redox process of the Ag<sup>+</sup>/Ag<sup>0</sup> and Ag<sup>0</sup>/Ag<sup>+</sup> species, proving the formation of AgNPs in the SiO<sub>2</sub>/GO hybrid material. Figure 2 shows the simultaneous determination of dopamine (DA) and epinephrine (EA) by the AgNPs/SiO2/GO/GCE electrode in PBS buffer, pH 7.0. It can be seen that the reduction peak currents for (DA), and (EA) increased proportionally with the concentration of dopamine and epinephrine in a range from 2.0 to 80 x 10-6 mol L-1, indicating that the AgNPs/SiO2/GO/GCE electrode can be used for the simultaneous determination of dopamine] and (i) versus [epinephrine] presented cathodic peak currents linearly proportional to increases in the concentration of dopamine and epinephrine (inset Figure 2). The limits of detection (LOD) of dopamine and epinephrine (isset Figure 2). The limits of detection (LOD) of dopamine and epinephrine were calculated as being, respectively, 0.26 µmol L<sup>-1</sup> and 0.27 µmol L<sup>-1</sup> performed according to IUPAC recommendations.



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# Designing electrochemically efficient Screen-printed sensors: Exploring the effect of electrochemical performance on electrode distance

Christopher W. Foster<sup>1</sup> and Craig E. Banks<sup>1</sup>

<sup>1</sup>Manchester Metropolitan University Faculty of Science and Engineering, School of Chemistry and the Environment, Division of Chemistry and Environmental Science, Manchester Metropolitan University, Chester Street, Manchester M15 GD, UK

Screen-printed electrodes have been a key area of research for many years within electrochemistry due to their ability to be mass produced, giving a high reproducibility and low costs which allow for one-shot sensors. Along with these attributes, they have the ability to be produced with many different geometries and designs, which can be suited for the application at hand. Creating a design can prove difficult as fundamental electrochemistry states that the Ohmic drop can lead to a reduced signal due to the distance between the reference and working electrode [1].

Recent literature by Tangkuaram [2] has explored the difference between six different electrode configurations, testing many scenarios for the three-electrode system. In this paper, the distances between the working, counter and reference electrode were altered with their effect explored upon the electrochemical response using a redox probe, but a systematic study was not performed. In this work, we elaborate upon this and test extreme distances between the electrodes and the overall effect upon their electrochemical capabilities, towards analytes such as potassium ferrocyanide and hexaammine-ruthenium chloride, with some staggering results, in terms of peak height, over potential and heterogeneous rate constants.



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# Direct Electrochemistry of Flavin-Dependent Oxidases Assembled on Electrochemically Reduced Graphene Oxide-Carbon Nanotubes Hybrid System for Glucose and Lactate Biosensing

Barbara Kowalewska, Katarzyna Jakubow Department of Chemistry, University of Warsaw Pasteura 1, PL-02-093 Warsaw, Poland bstar@chem.uw.edu.pl

Graphene oxide (GO) has a unique ability to form stable aqueous dispersions, highly bio-compatible and possess good electrocatalytic properties. In addition, its reductive product graphene is a unique material with potential applications in diverse fields and one of the hottest materials of interest. It was demonstrated that it is possible to prepare a water dispersible GO-multi-walled carbon nanotubes (MWCNTs) hybrid material via non-covalent  $\pi$ - $\pi$  stacking interactions [1]. Dispersing MWCNTs via non-covalent approaches cannot depress its intrinsic electrical, mechanical, and optical properties. The incorporation of GO with MWCNTs render this hybrid material as a versatile platform for the electrocatalytic applications. Conversely, the insulating property of GO caused by the aliphatic sp<sup>3</sup> hybridized domain, limits its conductivity. Therefore for improving the conductance, it can be reduced to graphene either by chemical, thermal or electrochemical methods. Recent studies as well reveal that the electrochemical reduction of GO to graphene (ERGO) was appreciably improved after the incorporation of MWCNTs.

Our research focuses on the direct electrochemical performance of glucose oxidase (GOx) and lactate oxidase (LOx) immobilized on ERGO/4-(pyrrole-1-yl) benzoic acid (PyBA) modified MWCNTs hybrid system. GOx and LOx are enzymes containing tightly bound flavin adenine dinucleotide (FAD) redox centers embedded deeply in the protein [2]. Modification of carbon nanotubes allow to obtain thin and organized films, causing a rapid and effective transfer of electrons between the active center of the biocatalyst (GOx or LOx) and the electrode surface. The presence of PyBA in our hybrid system significantly improves their stability and introduces new functional groups that have great importance in the enzyme immobilization process onto the ERGO/MWCNTs/PyBA-modified electrode [3].

In this work stable immobilization and direct electron transfer of oxidase enzymes were achieved on the hybrid system modified glassy carbon electrode. The resulting electrode gave a well-defined redox peaks with a formal potential of about -460 mV for GOx and -444 mV for LOx (vs. Ag/AgCl) in 0.1 phosphate buffer solution pH=7.0. Furthermore, the method for detecting of glucose and/or lactate was proposed based on the decrease of oxygen caused by the enzyme-catalyzed reaction between enzyme and substrate. The low calculated apparent Michaelis-Menten constant ( $K_M^{app}$ ) was 14.3 mM for GOx and 8.25 mM for LOx, implying the high enzymatic activity and affinity of immobilized enzyme for glucose and lactate, respectively. It can reasonably be expected that this observation might hold true for other noble carbon nanostructure-electroactive protein systems, providing a promising platform for the development of biosensors and biofuel cells.

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#### Copper Oxide-Modified Carbon Paste Electrode on determination of

#### Catechol

Luane Ferreira Garcia<sup>1</sup>; Michelle Pereira Quintino<sup>1</sup>; Stephen Rathinaraj Benjamin<sup>1</sup>; Aparecido Ribeiro de Souza<sup>2</sup>: Neemias Cintra Fernandes<sup>1</sup>: Eric de Souza Gil<sup>1</sup>

<sup>1</sup> Faculty of Pharmacy, Federal University of Goiás, Av. Universitária s/n, 74605-220 Goiânia, GO,

Brazil

<sup>2</sup> Institute of Chemistry, Federal University of Goiás, Campus Samambaia, CP 131 CEP 74001-970

Goiânia, GO, Brazil

Email:luane.fg@hotmail.com

The chemically modified electrodes (CMEs) present many advantages over conventional tools, and the resulting applications are intimately linked to the physicochemical properties of the modifier. One of the main advantages of CME is the enhancement of electrocatalytic properties, thereby increasing their sensitivity and selectivity. A wide variety of organic and inorganic compounds have been used for the preparation of modified electrodes. The use of non-noble transition metal oxides have attracted attention due its remarkable properties, i.e. low cost, mechanical and chemical stability, biocompatibility and simplicity to obtain nanostructured materials of large specific surface area (PRIYA and BERCHMANS, 2012). Moreover, the impregnation of metal oxides on graphite powder, usually employed in carbon paste electrodes (CPEs), may be very promising for the development of electrochemical sensors. Thus, the easy surface renewal of CPEs leads to higher reproducibility, whereas the inherent electrocatalytic activity of metallic modifiers might improve the sensitivity, also modulating the selectivity (VYTŘAS, et. al., 2009; PRIYA and BERCHMANS, 2012). Therefore, the aim of this work was modificate conventional carbon paste electrodes by using copper oxide in order to increase sensitivity in quantitative determinations of cathecol. The graphite powder was initially activated by oxidation with nitric acid, under reflux. Then, the impregnation of CuO on the activated carbon surface was achieved by addition of copper salts solutions (in various proportions), followed by drying overnight (80°C). Co-precipitation of copper cations was achieved by addition of a KOH/KNO3 solution at 90°C, followed by carbonization at 250°C for two hours under nitrogen atmosphere. The electrodic properties of the obtained CuO-CPEs were studied by voltammetry by using standard solutions of potassium ferrocyanide and catechol in a wide pH range (3.0; 5.0; 7.0 and 9.0). The capacitive current observed in phosphate buffer solutions (blank) for all CuO-CPEs (1, 2 and 5%) were lower than the observed for CPEs. On the other hand, the Faradaic currents observed for buffer solutions containing ferrocyanide or catechol was higher and exhibited higher reversibility for CuO-CPEs than for non-modified CPEs. Hence, it can be assumed that the impregnation of CuO on CPEs improves the electrode conductivity and its effective electroactive surface area. Moreover, the cyclic voltammograms obtained at different sweep rates (25-500 mV.s<sup>-1</sup>) in pH 7.0, 0.1 M phosphate buffer, containing 1 mM catechol, indicated that the peak current increased linearly with square root of sweep rate. The resulting linear correlation (r = 0.99886) indicates that the redox process is limited by diffusion rather than due electron transference. The differential pulse voltammetry (DPV), tested under a wide pH range, was used to evaluate the best response between different CuO-CPEs against catechol detection. Thus, the electrocatalytic efficiency of modified CPEs against catechol oxidation was higher for higher amounts of impregnated CuO. The quantitative determination of catechol at 5% CuO-CPEs, in pH 7.0, was achieved at concentrations ranging from 0.4 to 1.7  $\mu$ M (r = 0.9941), RSD < 5%. Therefore, it is concluded that the CPEs can be easily and inexpensively modified by CuO, leading to promising tools for environmental analysis of phenolic compounds.

Keywords: modified carbon paste electrodes; DPV; CV; phenolic compounds.

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#### Hot Electron-Induced Electrochemiluminescence at Carbon Electrodes

Kalle Salminen, Matti Pusa, Päivi Kuosmanen and Sakari Kulmala Aalto University Kemistintie 1, FI 00076 Aalto, Finland sakari.kulmala@aalto.fi

We have previously shown that thin insulating film-coated electrodes can be used to inject hot electrons into aqueous electrolyte solutions causing of a sequence of free radical reactions which can be utilsed to produce chemiluminescence.<sup>1</sup> Presently, we demonstrate that some compounds not excitable on the basis of traditional electrochemistry can be excited in aqueous solution at certain type of carbon paste electrodes which seem to naturally form a thin insulating film on top of them during the curing stage.

Aromatic Tb(III) chelates are used as an example of metal chelates that can be detected on time-resolved electrochemiluminescence measurements on the basis of their long-lasting emission.<sup>2</sup> These chelates provide a sensitive basis for bioaffinity assays in which Tb(III) chelates are used as electrochemiluminescent labels.

Fluoresceine<sup>3</sup> and rhodamine  $B^4$  are used as examples of organic luminophores displaying a short-lived cathodic electrochemiluminescene that are known to be excitable on the basis of hot electron electrochemistry at thin insulating film-coated electrodes in fully aqueous solutions, and also at the present electrode materials.

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# Influence of TiN Films with Different Thickness on LiFePO4/C Cathode Performance Using Magnetron Sputtering

Xiangyun Deng, Chen Chen, Lei Dong, Xifei Li, Dejun Li

Energy and Materials Engineering Center, Institute of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China Bin Shui West Road 393, Xi Qing District, Tianjin 300387, P. R. China Tel/Fax: +86-22-23766519; Email: d li1961@126.com

The commercial LiFePO<sub>4</sub> in lithium ion batteries has been suffering from its poor cycling performance. In this study, a magnetron sputtering technique was employed to surface modify a commercial LiFePO<sub>4</sub>/C cathode with various highly conductive thickness-controlled titanium nitride (TiN) films to enhance the cathode performance. The microstructure and compositions of modified LiFePO<sub>4</sub>/C samples were characterized by X-ray diffraction (XRD) and Raman spectroscopy, scanning electron microscopy (SEM). It was found that the uniform and dense TiN films were successfully formed onto the cathode electrodes via the magnetron sputtering method. Moreover, it is further disclosed that the improved electrochemical performance of modified LiFePO<sub>4</sub>/C electrode is highly dependent on the TiN film thicknesses. The TiN film with optimized thickness can effectively improve the battery performance of the commercial LiFePO<sub>4</sub>/C cathode. Electrochemical impedance spectroscopy (EIS) demonstrated that the performance improvement results from increased electrical conductivity of the cathode modified by magnetron sputtering derived TiN films.

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# CoO modified porous carbon anode enhancing electrochemical performance of Li-ion batteries

Dejun Li<sup>1</sup>, Yan Han<sup>1</sup>, Lei Dong<sup>1</sup>, Jianmin Feng<sup>1</sup>, Xifei Li<sup>1</sup>, Shuangxi Liu<sup>2</sup>

1, Energy and Materials Engineering Center, Institute of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China

2, Institute of New Catalytic Materials Science, College of Chemistry, Nankai University, Tianjin 300071,

China

Bin Shui West Road 393, Xi Qing District, Tianjin 300387, P. R. China Tel/Fax: +86-22-23766519; Email: dli1961@126.com

A cobalt oxide modified porous carbon has been synthesized via a facile solvothermal method followed by a simple thermal treatment process. Scanning electron microscopy and transmission electron microscopy images reveal that Co3O4 nanoparticles (NPs) with sizes of 20-40 nm are uniformly anchored onto porous carbon (PC). As an anode material for Li-ion batteries (LIBs), the composite exhibits enhanced reversible capacity, excellent cyclic performance, high Coulombic efficiency and good rate capability, which could be attributed to the 3D hierarchical porous structure of PC as well as the small size of the Co3O4 NPs providing convenient and accessible routs for electrolyte diffusion and intercalation of Li ions. Moreover, the interconnective networks of PC could decrease the inner resistance of LIBs and maintain structural stability. Thus the Co3O4/PC composite could be a promising anode material for high-performance LIBs.

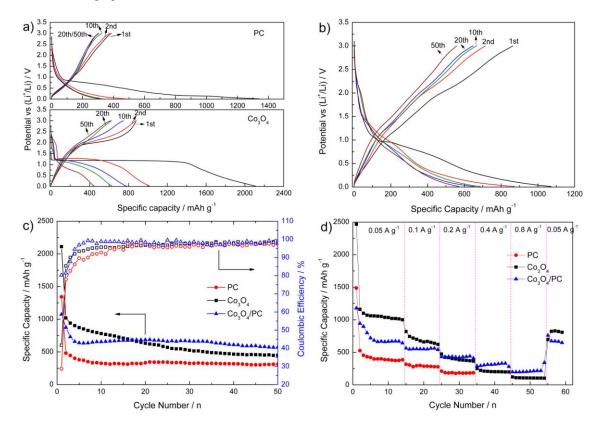


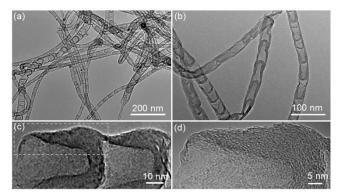
Fig. 7 Galvanostatic charge-discharge curves of the PC,  $Co_3O_4$  (a) and  $Co_3O_4/PC$  composite (b) cycled at the 1st, 2nd, 10th, 20th and 50th between 0.01 and 3 V (vs Li<sup>+</sup>/Li) at 100 mA g<sup>-1</sup>. (c) Cycling performance and (d) Rate capability for the PC,  $Co_3O_4$  and  $Co_3O_4/PC$  composite electrodes.

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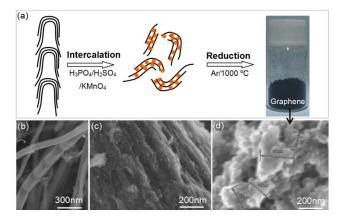
## Efficient Chemical Exfoliation of N-doped Graphene from Ncontaining Bamboo-like Carbon Nanotubes

Dejun Li, Jianmin Feng, Lei Dong, Yan Han, Xifei Li Energy and Materials Engineering Center, Institute of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China Bin Shui West Road 393, Xi Qing District, Tianjin 300387, P. R. China Tel/Fax: +86-22-23766519; Email: dli1961@126.com

N-doped graphene is prepared from N-containing carbon nanotubes (CNTs) by chemical exfoliation. The CNTs adopted for graphene are characterized by a discontinuous wall that consists of nano-size graphite layers, exhibiting a bamboo-like appearance. Take advantage of this characterization, the most time-consuming process of chemical oxidation that involves intercalation in graphene from CNT has been markedly reduced. The reduction in processing time is attributed to the diffusion distance of chemical oxidation intercalation into nano-size graphite composed of a bamboo-like carbon nanotube (BCNT) wall being far less than that of conventional chemical exfoliation into micro-size graphite. The efficiency of graphene fabrication from BCNT is twice higher than that from graphite. Transmission electron microscopy and scanning electron microscopy confirmed that the products were nano-size graphene. X-ray photoelectron spectroscopic analysis showed the presence of nitrogen in the crystal lattice of graphene



**Fig. 1** TEM images of BCNT (a, b). High-resolution TEM images of nanoshell consisting of BCNT (c). Enlarged view of the side wall of a nanoshell (d).



**Fig. 2** Schematic for graphene fabrication from BCNT (a) and SEM images from BCNT to graphene (b) BCNT, (c) oxidized BCNT, and (d) graphene.

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