Book of Abstracts of the

15th Topical Meeting of the International Society of Electrochemistry

Interfacial Electrochemistry at Atomic, Molecular and Nanoscale Domains

27-30 April 2014
Niagara Falls, Canada

Organized by:
ISE Division 6 Molecular Electrochemistry
ISE Division 7 Physical Electrochemistry
ISE Region Canada

International Society of Electrochemistry
Rue de Sébeillon 9b
1004 Lausanne
Switzerland

Printed in Canada

Organizing Committee

Chair

Aicheng Chen, *Canada*

Members

Carlos Frontana, *Mexico*
Enrique Herrero, *Spain*
Denis Kramer, *UK*
Jiri Ludvik, *Czech Republic*
Sasha Omanovic, *Canada*

Table of Contents

Oral presentation program

Welcome Message

On behalf of the International Society of Electrochemistry, I extend my warmest welcome to all of you to the 15th Topical Meeting in Niagara Falls, Canada. The theme of the meeting is "Interfacial Electrochemistry at Atomic, Molecular and Nanoscale Domains". This is the first topical meeting in Canada after a successful annual meeting in 2007 in Banff.

This meeting is intended to provide an opportunity for participants to convey and discuss in depth the most recent advancements in interfacial electrochemistry in theoretical as well as experimental and application areas, especially on the atomic, molecular and nanoscale levels. Recent surge of electrochemistry in energy related areas and analytical sensors require the fundamental knowledge in such levels. Therefore it is very timely and necessary to have this type of meeting.

Also, this meeting has a special meaning, to celebrate my dear friend Professor Jacek Lipkowski's 70th birthday this spring. As you know, he is renowned for groundbreaking research conducted over the past 30 years. And he was awarded the Electrochimica Acta Gold Medal of the International Society of Electrochemistry in Busan ISE Annual Meeting in 2005 which I was fortunate to organize. The Acta Gold Medal is the highest award of our society. Recently he was the recipient of the 2010 E.B. Yeager Award given by Electrochemical Society. Currently, he is expanding his interest to bio-related research on proteins and peptides. I am sure we will hear new findings from him for many years to come.

No doubt this will be a successful meeting not only in science, but also in making friends. Therefore, I'd like to give a big applause to Professor Aicheng Chen and his team for organizing this meeting.

I wish you enjoy the meeting and have a wonderful stay in Canada.

Hasuck Kim
President, International Society of Electrochemistry (ISE)

Program

ISE
INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY

Sunday

Strategy Room 3, Sheraton

15:00-15:10	Welcome
15:10-16:00	Jacek Lipkowski
16:00-16:20	Coffee
16:20-16:40	Juan Feliu
16:40-17:00	Shi-Gang Sun
17:00-17:20	Philip Bartlett
17:20-17:40	Zhong-Qun Tian
17:40-18:00	Robert Hillman
18:30-20:30	Getting Together

Monday

Niagara Room

08:00-08:40	N. J. Tao

	Niagara Room	**Brock Room**	**Elizabeth Room**
	Electrochemical surface processes	Electrochemical surface processes	Advanced imaging techniques
08:50-09:10	Marc Koper	Heinz-Bernh. Kraatz	Ulrich Stimming
09:10-09:30	Karin Leistner	Kagan Kerman	Josh Byers
09:30-09:50	Viola Birss	Samuel Perry	Heili Kasuk
09:50-10:10	Coffee Break		
	Electrochemical surface processes	Quantum chemical approaches and theoretical modeling	Advanced imaging techniques
10:10-10:30	Olaf Magnussen	Wolfgang Schmickler	Slawomir Sek
10:30-10:50	James Noel	Carl Albrecht Schiller	Jeffrey Shepherd
10:50-11:10	Steen Schougaard	Chia-Liang Sun	K.Andreas Friedrich
11:10-11:30	Jungsook Clara Wren	Michael Elkerling	Sergey Krachkovskiy
11:30-11:50	Xiaobo Ji	Marta Figueiredo	Bernhard Roling
11:50-12:10	Mark Orazem	Sara Panahian Jand	Pavel Janda
12:10-13:10	Lunch		
13:10--14:30	Journey Behind the Falls		
	Electrochemical surface processes	Adsorption and charge transfer	Organic and coordination electrochemistry
14:30-14:50	Clau. Buess-Herman	Janine Mauzeroll	Gregory Wildgoose
14:50-15:10	Nico Cousens	Sanela Martic	Felipe J. Gonzalez
15:10-15:30	Dominic Rochef	Zbigniew Stojek	Ayman Nafady
15:30-15:50	Minoru Umeda	Cassandra Ostrom	Jiri Ludvik
15:50-16:10	Coffee Break		
16:10-16:30	Mark McDermott	Renata Bilewicz	Tomas Mikysek
16:30-16:50	Ilia Valov	Tomohiro Higashi	Richard Webster
16:50-17:10	Sachiko Ono	Gilbert Noll	Weronika Lotowska
17:10-17:30	Abdelhafed Taleb	Andre Dourado	Andrea Mulas
17:30-17:50	Muge Civelekoglu	Michael Inkpen	Yongchun Zhu
17:50-19:00	Break		
19:00-21:00	Poster Session		

Tuesday

	Niagara Room
08:00-08:40	Masatoshi Osawa

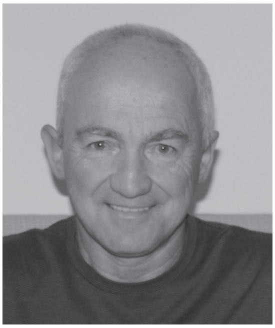
	Niagara Room	Brock Room	Elizabeth Room
	Electrochemical surface processes	Modern applications of interfacial electrochemistry	Spectroelectrochemistry
08:50-09:10	Carlos Frontana	Pawel J. Kulesza	Manuela Rueda
09:10-09:30	Susana de Torresi	Hasuck Kim	Wen-Feng Lin
09:30-09:50	Enrique Herrero	Sylvie Morin	J. Jay Leitch
09:50-10:10	Coffee Break		
	Electrochemical surface processes	Modern applications of interfacial electrochemistry	Spectroelectrochemistry
10:10-10:30	Peter Pickup	Thomas Doneux	Takamasa Sagara
10:30-10:50	Vitali Weissbecker	Hua-Zhong Yu	Bin Ren
10:50-11:10	Zhongwei Chen	Sasha Omanovic	Ladislav Kavan
11:10-11:30	Ewel. Bolimowska	Idriss Bakas	Ian Burgess
11:30-11:50	Antoine Depeuch	Richard Nichols	Wen-Bin Cai
11:50-12:10	Virginija Kepeniene	Zhigang Zhu	Jan Macak
12:10-13:30	Lunch		
	Electrochemical surface processes	Modern applications of interfacial electrochemistry	Spectroelectrochemistry
13:30-13:50	Bradley Easton	Xiaoyin Xiao	Dan Bizzotto
13:50-14:10	Valent. Lazarescu	Bing Joe Hwang	Miecz. Lapkowski
14:10-14:30	Ana C. Tavares	Elena Baranova	Fra. Prieto-Dapena
14:30-14:50	Heather A. Andreas	Roberto Torresi	YuYe J. Tong
14:50-15:10	Huamin Zhang	David Mitlin	Yan-Xia Jiang
15:10-15:30	Coffee Break		
15:30-15:50	Zhifeng Ding	Andy X. Sun	Boniface Kokoh
15:50-16:10	Alain Pailleret	Mei Cai	Piotr Pander
16:10-16:30	R. Ramanauskas	Lionel Santinacci	Ioa. Katsounaros
16:30-16:50	Sami Tuomi	Aiping Yu	Przemyslaw Data
16:50-17:10	Galyna Shul	Mitsuharu Chisaka	Jaroslaw Sar
17:10-17:30		Wojciech Nogala	Sylwia Zoladek
17:30-18:45	Break		
18:45-19:30	Cash Bar		
19:30-23:00	Banquet		

Wednesday

Niagara Room
Daniel Belanger

Niagara Room	Brock Room
Electrochemical surface processes	Modern applications of interfacial electrochemistry
Bagd. Kenzhaliev	Sook Mei Khor
Piret Pikma	Shuhui Sun
Matias Quiroga	Qiangfeng Xiao
Coffee Break	
Electrochemical surface processes	Modern applications of interfacial electrochemistry
Matthew Asmussen	Sayoko Shironita
Gary A. Attard	Xia Li
M. V. Sivaiah	Laurence Danis
Essen Suleimenov	Vlastimil Vyskocil
Stijn F. L. Mertens	Winston Doherty
Jinghua Guo	Aicheng Chen
Lunch	

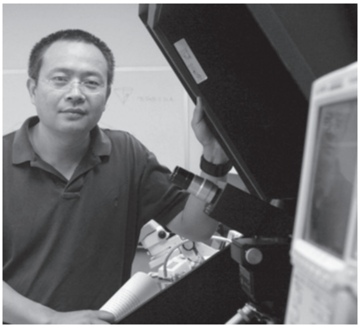
Keynote Speakers



Dr. Daniel Bélanger is currently Professor in the Département de Chimie de l'Université du Québec à Montréal. He completed his graduate studies in 1985 with Jean-Pol Dodelet at the Institut National de la Recherche Scientifique (INRS) and was a postdoctoral research associate with Mark S. Wrighton at the Massachusetts Institute of Technology (MIT). He has been invited professor at several schools in France and spent part of a sabbatical leave at Los Alamos National Laboratory in 1994, working with Shimshon Gottesfeld. He has made contributions in the area of biosensors based on immobilized enzyme in conducting polymers, electrochemical reduction of nitrate, chemical modification of surfaces by the diazonium chemistry and electrochemical capacitors. Professor Bélanger has published over 150 publications, which have been cited more than 6000 times and 1000 times per year in the recent years. He has given over 100 invited lectures worldwide. He is currently Associate Editor for Electrochemistry Communications. He sat on various grant selection committees in Canada and France.

Dr. Jacek Lipkowski is a Professor of Chemistry and Canada Research Chair at the University of Guelph, Guelph, Ontario, Canada. He received his PhD and DSc from the University of Warsaw, Poland and moved to Canada in 1983. His research interests span several areas such as electrochemistry, surface spectroscopy and biomimetics. He has authored about 200 papers and several book chapters. He serves as co-editor of a series "Advances in Electrochemical Sciences and Engineering". Professor Lipkowski is Fellow of the Royal Society of Canada, Killam Fellow and Fellow of the International Society of Electrochemistry (ISE). He is recipient of several awards including Gold Medal and Jaques Tacussel Prize of ISE, John Polanyi Award of the Canadian Society for Chemistry, Zawidzki Medal of the Polish Chemical Society and Alexander von Humboldt Stiftung Research Award.

Prof. Masatoshi Osawa received his BE (1974), ME (1976), and DE (1984) degrees in material science from Tohoku University, Sendai, Japan. He was an assistant professor (1976-1988) and an associated professor (1988-1994) of Tohoku University, and has been a full professor of Catalysis Research Center at Hokkaido University, Sapporo, Japan since 1994. He was also a visiting scientist at IBM San Jose Research Laboratories from 1984 to 1985. Prof. Osawa has made outstanding contributions in the field of physical electrochemistry through the development of Surface-Enhanced Infrared Absorption Spectroscopy. He has published ~170 refereed papers, reviews, and book chapters. He is recipient of several awards including Scientific Achievement Award from ECSJ (2001), Creative Research Award from the Chemical Society of Japan (2005), Jaques Tacussel Prize of ISE (2005), The Award of The Japan Society for Analytical Chemistry (2010), David C. Grahame Award from Physical and Analytical Division of ECS (2011), and The Award of ECSJ (2012). He serves on the Editorial Board of Journal of Electroanalytical Chemistry.



Professor Nongjian(NJ) Tao is the Director of the Center for Bioelectronics and Biosensors, Biodesign Institute at Arizona State University (ASU). He joined the ASU faculty as a professor of electrical engineering and an affiliated professor of chemistry and biochemistry in August 2001. He is an elected fellow of the American Association for the Advancement of Science and the American Physical Society. He has over 10 US patents, published over 200 refereed journal articles with h-index of 63, and given over 200 invited and keynote talks worldwide. He received Alexander von Humboldt Senior Research Award, Microscopy Today Innovation Award, Hellmuth Fisher Medal, National Science Foundation Special Creativity Award, Arizona Technology Enterprise Innovator of the Year, and Molecular Imaging Young Microscopist Award. His current research interests include chem- and bio-sensors, molecular and nanoelectronics, and mobile health devices and applications.

Sunday, 27 April 2014 - Afternoon

Strategy Room 3, Sheraton on the Falls

Chaired by: Aicheng Chen

15:00 to 15:10 Welcome

15:10 to 16:00 Keynote page 47

Jacek Lipkowski (Department of Chemistry, University of Guelph, Guelph, Canada)

Building a Biomimetic Membrane at an Electrode Surface

16:00 to 16:20 Coffee Break

Chaired by: Enrique Herrero and Sasha Omanovic

16:20 to 16:40 Invited page 81

Juan M. Feliu (Institute of Electrochemistry, Universidad de Alicante, Alicante, Spain), Enrique Herrero, Rubén Rizo, Elton Sitta

Towards the Understanding of Interfacial pH Scale at Pt(111) Electrodes

16:40 to 17:00 Invited page 165

Shi-Gang Sun (Chemistry Department, Xiamen University, Xiamen, China), Ling Chen, Chang-Deng Xu, Jin-Yu Ye, Chun-Hua Zhen, Zhi-You Zhou

Electrochemical *in situ* FTIR spectroscopic studies of adsorption processes on Pt single crystal planes and nanoparticles

17:00 to 17:20 Invited page 57

Philip Bartlett (Department of Chemistry, University of Southampton, Southampton, United Kingdom)

Plasmonic Electrode Structures for Electrochemical SERS

17:20 to 17:40 Invited page 170

Zhong-Qun Tian (State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, China)

Some Developments and Bottlenecks of Electrochemical Surface Raman Spectroscopy

17:40 to 18:00 Invited page 89

Robert Hillman (Department of Chemistry, University of Leicester, Leicester, United Kingdom), Robert Barker, Natalie Corden, Robert Dalgleish, Andrew Glidle, Karl Ryder, Rachel Sapstead, Maximilian Skoda, Erik Watkins

Lateral and Vertical Spatial Control of Electroactive Film Deposition for Latent Fingerprint Enhancement

18:30 to 20:30 Welcome reception at the Sheraton on the Falls Fallsview ABC

Monday 28 April 2014 - Morning

Niagara Room

Chaired by: Enrique Herrero

08:00 to 08:40 Keynote page 49

N.J. Tao (Center for Bioelectronics and Biosensors, Arizona State University, Tempe, USA)

Plasmonic-Based Electrochemical Current and Impedance Imaging

---

s3 Advanced imaging techniques

Elizabeth Room

Chaired by: Zhong-Qun Tian

08:50 to 09:10 Invited page 159

Ulrich Stimming (Institute for Advanced Study, Technische Universität München, Garching, Germany), Ueli Heiz, Jiwei Ma, Oliver Schneider, Lukas Seidl

SPM studies of intercalation mechanisms in electrode materials for Li-ion batteries at the nanoscale

09:10 to 09:30 page 64

Josh Byers (Chemistry, University of Warwick, Coventry, United Kingdom), Aleix Güell, Pat Unwin

Structure-Activity Relationships in Electrocatalysis at Individual Carbon Nanotubes using Scanning Electrochemical Cell Microscopy (SECCM)

09:30 to 09:50 page 95

Heili Kasuk (Institute of Chemistry, University of Tartu, Tartu, Estonia), Vitali Grozovski, Vladislav Ivaništšev, Enn Lust, Tavo Romann

Interesting adsorption patterns of adsorbed organic compounds at Bi(111) electrode studied by *in-situ* STM and impedance spectroscopy methods

09:50 to 10:10

Coffee Break

Chaired by: Ulrich Stimming and Jeffrey Shepherd

10:10 to 10:30 Invited page 154

Slawomir Sek (Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Warsaw, Poland), Michal Jamroz, Joanna Juhaniewicz, Jan Pawlowski

Interactions of Pore-Forming Peptides with Lipid Films

10:30 to 10:50 Invited page 155

Jeffrey Shepherd (Chemistry and Biochemistry, Laurentian University, Sudbury, Canada), Said Mahboob, Kirsten Swanson

Characterizing Zinc Electrodeposits Using AFM and Scaling Analysis

10:50 to 11:10 page 83

K. Andreas Friedrich (Institute of Technical Thermodynamics, German Aerospace Center, Stuttgart, Germany), Stefan Helmly, Renate Hiesgen, Tobias Morawietz

Comparative Studies of Conductive Nanostructures and Activation Properties in Solid Polymer Electrolytes

11:10 to 11:30 page 107

Sergey Krachkovskiy (Chemistry Department, McMaster University, Hamilton, Canada), Gillian Goward, Allen Pauric, Bartosz Protas, Athinthra Sethurajan

Accurate Characterization of Ion Transport Properties in Lithium Ion Battery Electrolytes Using *in Situ* NMR

11:30 to 11:50 page 146

Bernhard Roling (Department of Chemistry, University of Marburg, Marburg, Germany), Daniel Ebeling, Michael Gellert, Valon Lushta, Andre Schirmeisen, Julia Siebert-Krümpelmann

Nanoscale Electrochemical Characterization of Materials by Means of Spatially Resolved Electrostatic Force, Current and Strain Measurements

11:50 to 12:10 page 92

Pavel Janda (Department of Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry ASCR, Prague, Czech Republic), Hana Tarabkova

Gaseous Nanobubbles at Solid/Liquid Interface: Implications for Surface Nanomorphology and Interfacial Processes

s6 Electrochemical surface processes

Brock Room

Chaired by: Philip Bartlett

08:50 to 09:10 Invited page 106

Heinz-Bernhard Kraatz (Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Canada)

Electrochemical Studies of Protein Kinase Catalyzed Phosphorylations

09:10 to 09:30 Invited page 100

Kagan Kerman (Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Canada), Anthony Joseph Veloso

Electrochemical Detection of Multi-target Therapeutics in Alzheimer's Disease

09:30 to 09:50 page 138

Samuel Perry (Department of Chemistry, University of Southampton, Southampton, United Kingdom), Guy Denuault

Limitations of Probing the Oxygen Reduction Reaction on the Millisecond Timescale due to Adsorbed Oxygen

09:50 to 10:10

Coffee Break

s4 Quantum chemical approaches and theoretical modeling

Brock Room

Chaired by: Michael Eikerling and Wolfgang Schmickler

10:10 to 10:30 Invited page 152

Wolfgang Schmickler (Institute of Theoretical Chemistry, Ulm University, Ulm, Germany), Fernanda Juarez, Noelia Luque, Leila Mohammadzade, Paola Quaino

Double-layer properties of several modifications of carbon – a theoretical study

10:30 to 10:50 page 151

Carl Albrecht Schiller (Development, Zahner-elektrik GmbH & Co KG, Kronach, Germany), Christian Böhmer, Franz Richter, Patrik Schmuki

Modeling Dye Sensitized Solar Cells Based on Nano Tubes or Nano Rods - A New Transmission Line Approach

10:50 to 11:10 page 163

Chia-Liang Sun (Department of Chemistry and Material Engineering, Chang Gung University, Tao-Yuan, Taiwan), Po-Tuan Chen, Chun-Yi Chiu, Michitoshi Hayashi, Yuan-Han Huang, Jin-Ting Tsai

Efficient Oxygen Reduction Reaction on N-doped Graphene Nanoribbons: a Combined Theoretical and Experimental Study

11:10 to 11:30 Invited page 80

Michael Eikerling (Department of Chemistry, Simon Fraser University, Burnaby, Canada), Steven Rinaldo

Theory of Platinum Mass Balance in Catalyst Layers of PEM Fuel Cells

11:30 to 11:50 page 82

Marta Figueiredo (Chemistry Department, Aalto University, Helsinki, Finland)

Bi and CO coadsorption on Pt nanoparticles

11:50 to 12:10 page 136

Sara Panahian Jand (Institute of Electrochemistry, Ulm University, Ulm, Germany), Payam Kaghazchi

Structure of LiF on Graphene: The Role of Electrostatic Effects on Determining the Structure of Solid Electrolyte Interphase

s6 Electrochemical surface processes

Niagara Room

Chaired by: Pawel Kulesza

08:50 to 09:10 Invited page 105

Marc Koper (Leiden Institute of Chemistry, Leiden University, Leiden, Netherlands)

Electrochemistry of water at platinum – revisited

09:10 to 09:30 page 111

Karin Leistner (IMW, IFW Dresden, Germany,), Kenny Duschek, Sebastian Fähler, Ludwig Reichel, Heike Schlörb, Ludwig Schultz

Control of magnetism at the electrode/electrolyte interface

09:30 to 09:50 Invited page 59

Viola Birss (Department of Chemistry, University of Calgary, Calgary, Canada), Corie Horwood

Electrochemically Addressable Metal Nanoparticles Deposited in Short Tantalum Oxide Nanotubes

09:50 to 10:10

Coffee Break

Chaired by: Marc Koper and Mark Orazem

10:10 to 10:30 Invited page 117

Olaf Magnussen (Institute for Experimental and Applied Physics, Christian-Albrechts-University Kiel, Kiel, Germany)

Surface X-ray Scattering Studies of Electrochemical Growth at Solid-liquid and Liquid-liquid Interfaces

10:30 to 10:50 Invited page 128

James Noel (Chemistry, University of Western Ontario, London, Canada), David Shoesmith, Jared Smith, Zin Tun

In Situ Neutron Reflectometry Study of pH Effects on Hydrogen Absorption by Zirconium During Cathodic Polarization

10:50 to 11:10 Invited page 153

Steen Schougaard (Chimie, UQAM, Montreal, Canada), Murielle Carmant-Derival, Christian Kuss, David Lepage, Guoxian Liang, Ngoc Duc Trinh

Delithation and Relithiation Kinetics of the Olivine Li_xFePO_4 (0<x<1) System

11:10 to 11:30 Invited page 180

Jungsook Clara Wren (Chemistry, Western University, London, Canada), Mehran Behazin, Ahmed Musa

Oxide Growth Kinetics during Aqueous Corrosion of Co-Cr and Ni-Cr Alloys: Potential, pH and Temperature Dependences

11:30 to 11:50 Invited page 93

Xiaobo Ji (College of Chemistry and Chemical Engineering, Central South University, Changsha, China), Yingchang Yang

Cathodic Corrosion for Powder Materials

11:50 to 12:10 Invited page 133

Mark Orazem (Department of Chemical Engineering, University of Florida, Gainesville, USA), Morgan Harding, Bernard Tribollet, Vincent Vivier, Shao-Ling Wu

Coupling of Faradaic and Charging Currents in Impedance Spectroscopy

Monday 28 April 2014 - Afternoon

s1 Adsorption and charge transfer

Brock Room

Chaired by: Janine Mauzeroll and Heinz-Bernhard Kraatz

14:30 to 14:50 Invited page 119

Janine Mauzeroll (Department of Chemistry, McGill University, Montreal, Canada), A. Dowine Dea Bruijn, Philippe Dauphin Ducharme, Andrea Greschner, Kai Lin Lau, Fiora Rosati, Danielle Salvatore, Hanadi Sleiman, Violeta Toader

Modulation of Charge Transfer Across Double Stranded DNA by Site-Specific Incorporation of Copper bis-Phenanthroline Complexes

14:50 to 15:10 page 118

Sanela Martic (Chemistry, Oakland University, Rochester, USA), Hanna Trezeciakiewicz, Jose O. Esteves Villanueva

Electrochemical Detection of Tau-tau Protein Binding on Gold Surfaces

15:10 to 15:30 page 160

Zbigniew Stojek (Faculty of Chemistry, University of Warsaw, Warsaw, Poland), Edyta Matysiak, Anna Nowicka, Slawomir Sek

Physicochemical Characterization of DNA Films on Gold Surface Containing Nucleotides of Different-Length

15:30 to 15:50 page 134

Cassandra Ostrom (Department of Chemistry, Lakehead University, Thunder Bay, Canada), Aicheng Chen

Pd-Based Trimetallic Nanoparticles for Enhanced Hydrogen Storage

15:50 to 16:10

Coffee Break

Chaired by: Susana Cordoba de Torresi and Kagan Kerman

16:10 to 16:30 Invited page 58

Renata Bilewicz (Department of Chemistry, University of Warsaw, Warsaw, Poland), Elzbieta Jablonowska, Ehud Landau, Dorota Matyszewska, Jan Pawlowski, Slawomir Sek

Ordering of 2-Octadecanoylaminoacetic Acid at Air-Water and Solution-Au(111) Interfaces

16:30 to 16:50 page 88

Tomohiro Higashi (Graduate School of Engineering, Nagasaki University, Nagasaki, Japan), Takamasa Sagara

Faradaic Phase Transition of Adsorbed Viologens on HOPG Electrode Surface

16:50 to 17:10 page 130

Gilbert Nöll (Chemistry-Biology, Siegen University, Siegen, Germany)

The unique binding properties of the flavoprotein dodecin studied with AFM force spectroscopy, QCM-D, and SPR

17:10 to 17:30 page 78

Andre Dourado (Química Fundamental, Instituto de Química da Universidade de São Paulo, Sao Paulo, Brazil), Tércio Paulo, Daniel Rodrigues, Paulo Sumodjo, Márcia Temperini

Study of Cysteine Adsorption on Pt from Acid Media

17:30 to 17:50 page 91

Michael Inkpen (Department of Chemistry, Imperial College London, London, United Kingdom), Tim Albrecht, Nathan Fitzpatrick, Mario Lemmer, Nicholas Long

Single-molecule conductance of redox-active complexes using a novel automated I(s) STM methodology

s5 Organic and coordination electrochemistry

Elizabeth Room

Chaired by: Jiri Ludvik and Gregory Wildgoose

14:30 to 14:50 Invited page 179

Gregory Wildgoose (School of Chemistry, University of East Anglia, Norwich, United Kingdom), Andrew E. Ashley, David L. Hughes, Elliot J. Lawrence, Vasily S. Oganesyan

Electrochemical Studies of Lewis Acids for Small Molecule Activation

14:50 to 15:10 Invited page 85

Felipe J. González (Química, Centro de Investigación y de Estudios Avanzados del IPN, Mexico, Mexico), Pablo D. Astudillo, Carlos Frontana, Miguel A. González-Fuentes, Drochss P. Valencia

Electrochemical and Chemical Formation of a Proton Transfer Complex Between the Quinone Dianion and Hydroquinone

15:10 to 15:30 page 126

Ayman Nafady (Department of Chemistry, King Saud University, Riyadh, Saudi Arabia), Alan Bond

Synthesis, Characterization, and Utilization of Metal-TCNQ Nanostructured Materials in Graphene-Based Flexible Energy Storage Devices

15:30 to 15:50 page 115

Jiri Ludvik (Molecular Electrochemistry, J. Heyrovský Institute of Physical Chemistry, Prague 8, Czech Republic), Irena Hoskovcova, Radka Metelkova, Miroslav Polasek

Electroreduction and dimer formation of Fischer Cr(0)-aminocarbene complexes with heterocyclic substituents

15:50 to 16:10

Coffee Break

Chaired by: Jiri Ludvik and Carlos Frontana

16:10 to 16:30 page 122

Tomas Mikysek (Department of Analytical Chemistry, University of Pardubice, Faculty of Chemical Technology, Pardubice, Czech Republic), Jiri Ludvik, Karel Vytras

Electrochemistry of Ferrocene Based Charge-Transfer Chromophores Containing Various Bridging Units

16:30 to 16:50 page 177

Richard Webster (School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore), Melvyn Lee, Malcolm Tessensohn

Using the Voltammetric Behavior of Vitamin K1 and Other Quinones to Estimate Relative Hydrogen-Bonding Strengths of Donor Compounds

16:50 to 17:10 page 189

Weronika Lotowska (Department of Chemistry, University of Warsaw, Warsaw, Poland), Katarzyna Brzostek, Marta Gierwatowska, Barbara Kowalewska, Pawel J. Kulesza, Adrianna Raczkowska, Iwona A. Rutkowska, Ewelina Seta, Ewelina Szaniawska, Sylwia Zoladek

Development of Biofilm-Supported Hybrid Electrocatalytic Materials for Biosensing and Bioenergetics

17:10 to 17:30 page 125

Andrea Mulas (Institut des Sciences Chimiques, Université de Rennes 1, Rennes, France)

Fast Redox Communication at Organometallic Carbon-rich Ruthenium Complexes Self-Assembled Monolayers

17:30 to 17:50 page 186

Yongchun Zhu (Department of Chemistry, College of Chemistry and Life Sciences, Shenyang Normal University, Shenyang, China), Amin Bao, Ying Gao, Qingxiao Jiang, Nan Xiao, Shigang Xin

Quantum chemical study on electrochemical catalytic oxidation of p-amino phenol at p-amino phenol modified graphite electrode with diazo-reaction

s6 Electrochemical surface processes

Niagara Room

Chaired by: Dominic Rochefort and Claudine Buess-Herman

14:30 to 14:50 Invited page 62

Claudine Buess-Herman (Service de Chimie Analytique et Chimie des Interfaces, Université Libre de Bruxelles, Bruxelles, Belgium), Jennifer Christophe, Thomas Doneux, Anne Meunier, Roman Michez, Stéphanie Vanderaspoilden

Electrochemistry in non-conventional electrolytes: case of the [BMIm][DCA] room temperature ionic liquid - gold interface

14:50 to 15:10 Invited page 72

Nico Cousens (Chemistry, University of Oxford, Oxford, United Kingdom), Florian Hausen, Kevin Lovelock, Susan Perkin, Alexander Smith

Ionic Liquid Structure at Mica and Graphene Interfaces

15:10 to 15:30 Invited page 145

Dominic Rochefort (Chemistry, Université de Montréal, Montréal, Canada), John Forgie, Bruno Gélinas, Han Jin Xie

Electrochemisty of Electroactive Ionic Liquids Modified with Ferrocene Redox Centers

15:30 to 15:50 page 174

Minoru Umeda (Department of Materials Science and Technology, Nagaoka University of Technology, Niigata, Japan), Hayato Itaya, Sayoko Shironita

H_2O_2 and Fe^{2+}-Induced Pt Electrode Dissolution in H_2SO_4 Solution

15:50 to 16:10

Coffee Break

Chaired by: Mark McDermott and Jungsook Clara Wren

16:10 to 16:30 Invited page 120

Mark McDermott (Chemistry, University of Alberta, Edmonton, Canada), Rongbing Du

Fabrication and Applications of Carbon Nano-band Electrodes

16:30 to 16:50 page 175

Ilia Valov (Electronic Materials (PGI-7), Research Centre Juelich, Juelich, Germany), Masakazu Aono, Tsuyoshi Hasegawa, Alpana Nayak, Tohru Tsuruoka, Rainer Waser

Interfacial Electrochemical Processes at the Atomic Scale. Nucleation, Charge Transfer and Imaging

16:50 to 17:10 page 132

Sachiko Ono (Department of Applied Chemistry, Kogakuin University, Tokyo, Japan)

Effect of Nanotopography of Aluminum Surface and Crystal Orientation on Pore Initiation of Anodic Porous Alumina

17:10 to 17:30 page 166

Abdelhafed Taleb (Chimie, UPMC - LECIME/ENSCP/ CNRSUMR7575, Paris, France), Pierre Dubot, Xue Yanpeng

Self-Assembled Gold Nanoparticles as Nanelectrocatalyst Templates for Surface Nanostructuring

17:30 to 17:50 page 70

Muge Civelekoglu (Chemistry, Istanbul Technical University, Maslak, Turkey)

Preparation and Characterization of Conducting Polymer (PANI) Decorated by Functionalized Multiwall Carbon Nanotubes

Tuesday, 29 April 2014 - Morning

Niagara Room

Chaired by: Jiri Ludvik

08:00 to 08:40 Keynote page 48

Masatoshi Osawa (Catalysis Research Center, Hokkaido University, Sapporo, Japan), Takaya Ishino, Akihiro Morita, Kenta Motobayashi, Akira Yamakata

Water and Ions at the Electrochemical Interface Studied by Surface-Enhanced Infrared Absorption Spectroscopy

---

s2 Spectroelectrochemistry

Elizabeth Room

Chaired by: Shi-Gang Sun

08:50 to 09:10 Invited page 147

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

FT-IR Spectroelectrochemical Study of Adenine and Thymine Adsorptions and co-Adsorption on Gold Electrodes: The Influence of pH

09:10 to 09:30 Invited page 114

Wen-Feng Lin (School of Chemistry & Chemical Engineering, Queens University Belfast, Belfast, United Kingdom)

New Insight into Electrocatalysis for Direct Alcohol Fuel Cells at Electronic, Atomic and Molecular Levels

09:30 to 09:50 page 112

J. Jay Leitch (Chemistry, University of Guelph, Guelph, Canada), Kyrylo Bessonov, Christa Brosseau, John Dutcher, Jacek Lipkowski, Sharon Roscoe

Voltage Induced Changes in the Structure of the Cholera Toxin B Subunit Bound to a Model Membrane

09:50 to 10:10

Coffee Break

Chaired by: Takamasa Sagara and Ian Burgess

10:10 to 10:30 Invited page 148

Takamasa Sagara (Division of Chemistry and Materials Science, Graduate School of Engineering, Nagasaki University, Nagasaki, Japan), Shoma Murakawa, Ken Ozera, Hironobu Tahara

Potential-Driven Dynamics of Ultra-Thin Liquid Films on Au(111) Electrode

10:30 to 10:50 Invited page 144

Bin Ren (Department of Chemistry, Xiamen University, Xiamen, China), Sheng-chao Huang, Teng-Xiang Huang, Mao-Hua Li, Xiao-Bing Lian, Zhi-Cong Zeng, Jin-Hui Zhong

In situ Raman Spectroscopy for Electrochemical Interfaces

10:50 to 11:10 page 97

Ladislav Kavan (Electrochemical Materials, J. Heyrovsky Institute of Physical Chemistry, Prague 8, Czech Republic), Otakar Frank, Barbora Laskova, Marketa Zukalova

Lithium Insertion into Titanium Dioxide: Electrochemistry, Raman Spectra and Isotope (Li, O) Labeling

11:10 to 11:30 Invited page 63

Ian Burgess (Department of Chemistry, Saskatoon, Canada), Mike Lardner, Scott Rosendahl, Kaiyang Tu

Spectroelectrochemistry Using Synchrotron Infrared Radiation

11:30 to 11:50 Invited page 66

Wen-Bin Cai (Department of Chemistry, Fudan University, Shanghai, China), Yao-Yue Yang

Surface-enhanced Infrared Spectroscopic Investigation of Reactions of Methanol and Ethanol at Pd Electrodes in Alkaline Media

11:50 to 12:10 page 116

Jan Macak (Department of General and Inorganic Chemistry, University of Pardubice, Pardubice, Czech Republic), Max Fraenkl, Deepak Patil, Koichi Shimakawa, Tomas Wagner, Vitezslav Zima

New approach of data mining from the complex impedance plane: parameters you have always wanted to have

s6 Electrochemical surface processes

Niagara Room

Chaired by: Juan Feliu

08:50 to 09:10 page 86

Sébastien Garbarino (Energie Matériaux Télécommunications, INRS, Varennes, Canada)

On the use of porous and preferentially oriented 100 Pt electrode in electrocatalysis

09:10 to 09:30 page 71

Susana Cordoba de Torresi (Instituto de Quimica, Universidade de São Paulo, Sao Paulo, Brazil), Raphael Colombo, Vinicius Gonçales, Denise Petri

Structuration of gold macropatterns over conducting and non-conducting substrates

09:30 to 09:50 page 87

Enrique Herrero (Instituto de Electroquímica, Universidad de Alicante, Alicante, Spain), Juan M. Feliu, Adolfo Ferre-Vilaplana, Juan V. Perales

Formic Acid Oxidation Mechanism on Platinum Electrodes

09:50 to 10:10

Coffee Break

Chaired by: Daniel Bélanger and Peter Pickup

10:10 to 10:30 Invited page 139

Peter Pickup (Chemistry, Memorial University, St. Johns, Canada), Reza Moghaddam

The Effects of Conducting Polymers on Formic Acid Oxidation at Pt Nanoparticles

10:30 to 10:50 page 178

Vitali Weissbecker (Institute of Energy and Climate Research IEK-3, Forschungszentrum Jülich GmbH, Jülich, Germany), Werner Lehnert, Klaus Wippermann

Electrochemical Impedance Spectroscopy on Metallic Materials for Bipolar Plate Application in HT-PEFC

10:50 to 11:10 Invited page 68

Zhongwei Chen (Chemical Engineering, University of Waterloo, Waterloo, Canada)

Advanced Catalysts for Oxygen Reduction Reaction in PEM Fuel Cells

11:10 to 11:30 page 61

Ewelina Bolimowska (CEA-Liten/CNRS-C2P2, Université de Lyon, Institut de Chimie de Lyon, Grenoble, France)

Investigation of the solid electrolyte interphase between graphite electrode/ ionic liquid electrolyte

11:30 to 11:50 page 54

Antoine Bach Delpeuch (Applied Electrochemistry, Fraunhofer Institut für Chemische Technologie ICT, Pfinztal, Germany), Marian Chatenet, Carsten Cremers, Jens Tübke

DEMS study: Ethanol and acetaldehyde stripping on Pt/C electrocatalyst at room temperature

11:50 to 12:10 page 99

Virginija Kepeniene (Department of Catalysis, Center for Physical Sciences and Technology, Vilnius, Lithuania), Jürаé Vaiciüniené, Rokas Kondrotas, Vidas Pakštas, Loreta Tamašauskaité-Tamašiünaitè, Eugenijus Norkus

Graphene and Niobium Oxide/Graphene Supported Platinum-Cobalt Nanocomposites as Electrocatalystsfor the Oxidation of Ethanol

s7 Modern applications of interfacial electrochemistry

Brock Room

Chaired by: Viola Birss

08:50 to 09:10 Invited page 108

Pawel J. Kulesza (Department of Chemistry, University of Warsaw, Warsaw, Poland), Justyna Orlowska, Iwona A. Rutkowska

Enhancement of transport rates by incorporation of noble metal nanoparticles to iodine/iodide based ionic liquid charge relays

09:10 to 09:30 Invited page 102

Hasuck Kim (Department of Energy Systems, DGIST, Daegu, Korea), Yang-Rae Kim, Jeong-Wook Oh, Hyo-Ju Seo

Molecular Level Electrogenerated Chemiluminescence for Protein Analysis

09:30 to 09:50 Invited page 124

Sylvie Morin (Chemistry, York University, Toronto, Canada)

Preparation and Characterization of Nanostructured Electrode Materials

09:50 to 10:10

Coffee Break

Chaired by: Richard Nichols and Hua-Zhong Yu

10:10 to 10:30 Invited page 77

Thomas Doneux (Chimie Analytique et Chimie des Interfaces, Université Libre de Bruxelles, Bruxelles, Belgium), Claudine Buess-Herman, Aurore De Rache, Anne Meunier, Marc Steichen, Eléonore Triffaux

Control and Optimisation of the Interfacial Architecture of Electrochemical DNA Biosensors

10:30 to 10:50 Invited page 184

Hua-Zhong Yu (Department of Chemistry, Simon Fraser University, Burnaby, Canada)

Electrochemical Heterogeneity in "Ideally Behaved" Redox Self-Assembled Monolayers

10:50 to 11:10 page 131

Sasha Omanovic (Department of Chemical Engineering, McGill University, Montreal, Canada), Mahdi Dargahi, Mari T. Kaartinen, Aisha Mousa, Valentin Nelea

Electrochemical Immobilization of Fibronectin on a Gold Surface: Control of Its Surface Conformation and Interaction with Endothelial Cells

11:10 to 11:30 page 55

Idriss Bakas (Department of Chemistry, University Paris Diderot, Paris, France), Mohamed M. Chehimi

Molecularly Imprinted Polymer Grafts through Interfacial Chemistry of Aryl Diazonium Salts for Highly Selective and Sensitive Electrochemical Sensors

11:30 to 11:50 Invited page 127

Richard Nichols (Department of Chemistry, University of Liverpool, Liverpool, United Kingdom), Simon Higgins, Jan Jeppesen, Nicola Kay, Edmund Leary, Jess Lycoops, Jens Ulstrup

STM Studies of Electrochemical Single Molecule Transistors

11:50 to 12:10 Invited page 187

Zhigang Zhu (School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai, China), Andrew J. Flewitt, William I. Milne, Francis Moussy, Huaqing Xie

Micro- and Nano- Approaches for Biosensing Applications

Tuesday 29 April 2014 - Afternoon

s2 Spectroelectrochemistry

Elizabeth Room

Chaired by: Dan Bizzotto and YuYe J. Tong

13:30 to 13:50 Invited page 60

Dan Bizzotto (Department of Chemistry, University of British Columbia, Vancouver, Canada)

Characterizing fluorophore labeled DNA-SAMs using electrochemical induced orientation changes and impedance methods

13:50 to 14:10 page 109

Mieczyslaw Lapkowski (Department of Physical Chemistry of Polymers, Silesian University of Technology, Gliwice, Poland), Juozas Grazulevicius, Sandra Pluczyk, Renji Reghu

Electrochemistry and spectroelectrochemistry of bipolar perylene diimide derivatives

14:10 to 14:30 page 141

Francisco Prieto-Dapena (Physical Chemistry, University of Seville, Seville, Spain), J. Jay Leitch, Jacek Lipkowski, Manuela Rueda, Zhang Fei Su

Quantitative SNIFTIRS study of the adsorption of adenine on Au(111) electrodes

14:30 to 14:50 page 171

YuYe J. Tong (Department of Chemistry, Georgetown University, Washington, USA), Thomas C. Allison, Dianne O. Atienza, DeJun Chen

In situ SEIRAS Investigation of Methanol Oxidation Reaction on PtRu Alloy and Ru@Pt Core-Shell NPs: New Insights on an Old Story

14:50 to 15:10 page 94

Yan-Xia Jiang (Department of Chemistry, Xiamen University, Xiamen, China)

In Situ Electrochemical FTIRS Study of Ethanol Electrooxidation on Cubic PtRh Alloys Supported on Graphene

15:10 to 15:30

Coffee Break

Chaired by: Boniface Kokoh and Robert Hillman

15:30 to 15:50 Invited page 103

Boniface Kokoh (Department of Chemistry, University of Poitiers, Poitiers, France)

Analytical Determination of the Reaction Products Resulted from Organics Electrooxidation on Various Nanomaterials

15:50 to 16:10 page 137

Piotr Pander (Faculty of Chemistry, Silesian University of Technology, Gliwice, Poland), Przemyslaw Data

Electrodeposited Polymers from Triphenylamine-Based Hydrazones as Electronically Active Materials

16:10 to 16:30 page 96

Ioannis Katsounaros (Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA), Alexander A. Auer, Angel Cuesta, Karl J. J. Mayrhofer, Wolfgang B. Schneider

Electrochemistry of Hydrogen Peroxide and its Essential Role in the Oxygen Reduction Reaction

16:30 to 16:50 page 73

Przemyslaw Data (Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland), Radoslaw Motyka, Piotr Pander

Novel Selenophene and Tellurophene Derivatives From Electrochemistry to Working Devices

16:50 to 17:10 page 150

Jaroslaw Sar (LEPMI, UMR 5279 CNRS, Grenoble University, St. Martin d'Hères, France), Amélia Almeida, Laurent Dessemond, Elisabeth Djurado

Graded and Homogeneous CGO/LSCF Cathode for IT-SOFC

17:10 to 17:30 page 188

Sylwia Zoladek (Department of Chemistry, University of Warsaw, Warsaw, Poland), Pawel J. Kulesza, Iwona A. Rutkowska

Interfacial functionalization of nanostructured metal nanoparticles: from changes in spectrochemical identity to enhancement of electrocatalytic properties

s6 Electrochemical surface processes

Niagara Room

Chaired by: E. Bradley Easton and Heather A. Andreas

13:30 to 13:50 Invited page 79

E. Bradley Easton (Faculty of Science (Chemistry), University of Ontario Institute of Technology, Oshawa, Canada), O Rian Reid, Farhana Saleh

The use of EIS measurements to determine the electrochemically active surface area of Pt

13:50 to 14:10 page 110

Valentina Lazarescu (Institute of Physical Chemistry Ilie Murgulescu, Romanian Academy, Bucharest, Romania), Mihai Anastasescu, Gianina Dobrescu, Mirela Enache, Mihail F. Lazarescu, Catalin Negrila, Loredana Preda

Field - Dipole Interactions in L-Cysteine-Thiolate Self Assembled at p- and n-GaAs(100) Electrodes

14:10 to 14:30 page 167

Ana C. Tavares (Energie, Materiaux et Telecommunications, Institut National de la Recherche Scientifique, Varennes, Canada), Willyam R. P. Barros, Marcos R. V. Lanza, Shuhui Sun

Oxygen Reduction on Fe_3O_4 nanoparticles supported on Printex Carbon and on Graphene

14:30 to 14:50 page 50

Heather A. Andreas (Department of Chemistry, Dalhousie University, Halifax, Canada)

Self-discharge in Manganese Oxide Electrodes for Neutral-Aqueous-Electrochemical Capacitors

14:50 to 15:10 page 185

Huamin Zhang (Division of Energy Storage, Dalian Institute of Chemical Physics,CAS, Dalian, China), Hexiang Zhong

Research and Development of Non-Pt Electrocatalysts for Proton Exchange Membrane Fuel Cells

15:10 to 15:30

Coffee Break

Chaired by: Carlos Frontana and Zhifeng Ding

15:30 to 15:50 Invited page 75

Zhifeng Ding (Chemistry, The University of Western Ontario, London, Canada)

$CuInS_2$ and Cu_2ZnSnS_4 Nanocrystal Inks for Thin Film Solar Cells

15:50 to 16:10 page 135

Alain Pailleret (Laboratoire Interfaces et Systèmes Electrochimiques (LISE, UPR 15), University Pierre and Marie Curie, Paris, France), Florence Billon, Catherine Debiemme-Chouvy, Claude Deslouis, Jean Gamby

Amorphous carbon nitride thin films: versatile electrode materials with interdependent properties at the nanoscale

16:10 to 16:30 page 143

Rimantas Ramanauskas (Electrochemical Materials Sciences, Center for Physical Sciences and Technology, Vilnius, Lithuania), Laima Gudaviciute, Olga Girciene, Aleksandr Kosenko

On the Properties of Anodic Oxide Films of Nanostructured Zn and Zn Alloy Coatings

16:30 to 16:50 Invited page 173

Sami Tuomi (Department of Chemistry, Aalto University, Espoo, Finland), Tanja Kallio

Low-Cost Molybdenum Sulfide and Carbide Catalysts for Hydrogen Evolution

16:50 to 17:10 page 157

Galyna Shul (Département de Chimie, Université du Québec à Montréal, Montréal, Canada), Daniel Bélanger

Formation of Ultrathin Electroactive Film on Carbon Surface from 1,10-Phenantroline in Acidic Electrolyte

17:10 to 17:30 page 84

Carlos Frontana (Centro de Investigación y Desarrollo Tecnológico en Electroquimica, Parque Tecnológico Querétaro S/N, Sanfandila, Mexico), Rutely Burgos-Castillo, Eduardo Martínez-González

Local Reactivity Indexes for Describing Changes in Properties during Electron Transfer Processes

s7 Modern applications of interfacial electrochemistry

Brock Room

Chaired by: Roberto Torresi and Olaf Magnussen

13:30 to 13:50 Invited page 182

Xiaoyin Xiao (Department of Biosensors and Nanomaterials, Sandia National Labs, Albuquerque, USA), Daniel Koleske, Ping Lu, Art Fischer, Richard Schneider, George Wang

Laser assisted photoelectrochemical etching of InGaN quantum structures

13:50 to 14:10 Invited page 90

Bing Joe Hwang (Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan), Delele Worku Ayele, Yi-Hsiu Chen, Felix Felix, Sunny Hy, John Rick, Wei-Nien Su, Han-Ping Tseng

Interfacial Phenomena of Battery Electrodes Investigated by Surface Enhanced Raman Spectroscopy

14:10 to 14:30 Invited page 56

Elena Baranova (Chemical and Biological Engineering, University of Ottawa, Ottawa, Canada), Anis Allagui, Spyridon Ntais, Saad Sarfraz

Ammonia electrooxidation on bimetallic PtIr and NiPd nanoparticles in alkaline media

14:30 to 14:50 page 172

Roberto Torresi (Instituto de Química, Universidade de São Paulo, São Paulo, Brazil), Tânia Benedetti, Pedro Camargo, Ricardo Fernandez, Flavia Reis

Electrochemistry of hybrid TiO_2/PANI thin films employing ionic liquids as electrolytes

14:50 to 15:10 Invited page 123

David Mitlin (Chemical and Materials Engineering, University of Alberta, Edmonton, Canada)

Microstructural Design of Nanoarchitectures for Energy Storage

15:10 to 15:30

Coffee Break

Chaired by: Andy X. Sun and Hasuck Kim

15:30 to 15:50 Invited page 162

Andy X. Sun (Mechanical and Materials Engineering, University of Western Ontario, London, Canada), Mei Cai, Xifei Li, Jian Liu

Applications of Atomic Layer Deposition for Li Ion Batteries

15:50 to 16:10 Invited page 65

Mei Cai (CMS, General Motors, Warren, USA)

Size-dependent Reduction to Synthesize Hierarchical Porous Si Particles with Reversible Morphology Evolution

16:10 to 16:30 page 149

Lionel Santinacci (Center for Interdisciplinary Nanoscience of Marseille, Aix-Marseille University, CNRS, Marseille, France), Loic Assaud, Elena Baranova, Nicolas Brazeau, Margrit Hanbucken, Vasile Heresanu, Kristina Pitzschel

Improved carbon-carbon bond splitting using Pd catalysts grown by atomic layer deposition onto TiO_2 nanotubes

16:30 to 16:50 Invited page 183

Aiping Yu (Department of Chemical Engineering, University of Waterloo, Waterloo, Canada)

Carbon Nanomaterials Supported $Ni(OH)_2$/NiO Hybrid Flower Structure for Supercapacitor

16:50 to 17:10 page 69

Mitsuharu Chisaka (Department of Electronics and Information Technology, Hirosaki University, Hirosaki, Japan), Yuta Ando, Hirokazu Muramoto

Titanium Oxynitride Supported on Graphene-Based Carbon Sheets as Oxygen Reduction Reaction Catalyst in Acid Media

17:10 to 17:30 page 129

Wojciech Nogala (Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland), Sylwester Gawinkowski, Martin Jönsson-Niedziolka, Magdalena Kominiak, Marcin Opallo, Kannan Palanisamy

Automated Patterning of Bare Metallic Nanostructures by Precisely Localized Electrorefining

Wednesday, 30 April 2014 - Morning

Niagara Room

Chaired by: Sasha Omanovic

08:00 to 08:40 Keynote page 46

Daniel Bélanger (Chimie, Université du Québec à Montréal, Montréal, Canada)

Modification of electrodes by electrochemical reduction of diazonium ions

---

s6 Electrochemical surface processes

Niagara Room

Chaired by: Sylvie Morin

08:50 to 09:10 page 98

Bagdaulet Kenzhaliev (Innovation sciences, Kazakh-British Technical University, Almaty, Kazakhstan)

Electrochemical Method for Extracting Non-Ferrous and Precious Metals from Refractory Materials Using Combined Reactions

09:10 to 09:30 page 140

Piret Pikma (Institute of Chemistry, University of Tartu, Tartu, Estonia), Vitali Grozovski, Enn Lust

In situ STM studies of Cd(0001) electrode in aqueous electrolyte solution

09:30 to 09:50 page 142

Matias Quiroga (Laboratoire de Réactivité et de Chimie des Solides (LRCS), Université de Picardie Jules Verne & CNRS, Amiens, France)

A new model of non-equilibrium electrochemical interfaces in electrochemical energy conversion

09:50 to 10:10

Coffee Break

Chaired by: James Noel and Elena Baranova

10:10 to 10:30 page 52

Matthew Asmussen (Chemistry and Surface Science, University of Western Ontario, London, Canada), Jeff Binns, Pellumb Jakupi, David Shoesmith

Electrochemical Impedance Spectroscopy Investigation of Microstructural Effects on the Corrosion of Mg Alloys

10:30 to 10:50 page 53

Gary Attard (School of Chemistry, Cardiff University, Cardiff, United Kingdom), Ashley Brew, Katherine Hunter, Jonathan Sharman, Edward Wright

Specific adsorption of perchlorate anions and Nafion® on Pthkl: their influence on the Oxygen Reduction Reaction

10:50 to 11:10 page 158

M.V. Sivaiah (Energetics Research Institute (EnRI), Nanyang Technological University, Singapore, Singapore), D. Abirami, H.G. Ang

Electrocatalytic properties of RuO_2 nanocomposite for hydrogen evolution reaction

11:10 to 11:30 page 161

Essen Suleimenov (Laboratory of Advanced Materials and Technology, Kazakh British Technical University, Almaty, Kazakhstan)

Influence of the electrochemical reaction between the components of the gas phase and the oxide melt on the structure of oxide systems

11:30 to 11:50 page 121

Stijn F. L. Mertens (Institut für Angewandte Physik, TU Wien, Vienna, Austria), Steven De Feyter, Thomas Greber, Adrian Hemmi, Rafael Küng, Stefan Muff, Jürg Osterwalder

An All-Inorganic Responsive Surface: Reversible Electrochemical Contact Angle Switching of Hexagonal Boron Nitride Nanomesh

11:50 to 12:10 page 121

Jinghua Guo (Advance Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA , USA), Yi-Sheng Liu, Per-Ander Glans

Enabling in-situ/in-operando soft X-ray spectroscopy for the catalytic and electrochemical reactions

s7 Modern applications of interfacial electrochemistry

Brock Room

Chaired by: Carlos Frontana

08:50 to 09:10 page 101

Sook Mei Khor (Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia), Yatimah Alias, Nadiya Darwish

An Electrochemical Sensing Interface for Dengue Virus Detection

09:10 to 09:30 Invited page 165

Shuhui Sun (INRS-Center for Energy and Materials, University of Quebec, Montreal, Canada), Mei Cai, Jean-Pol Dodelet, Ruying Li, Xueliang Sun, Gaixia Zhang

One-dimensional Pt Nanostructured Electrocatalysts for PEM Fuel Cell Applications

09:30 to 09:50 page 181

Qiangfeng Xiao (CMS, General Motors, Warren, USA)

Ultrathin Pt_xNi_{1-x} Nanowires: Tunable Composition and Electro Electrocatalytic Properties

09:50 to 10:10

Coffee Break

Chaired by: Aicheng Chen and Steen Schougaard

10:10 to 10:30 page 156

Sayoko Shironita (Department of Materials Science and Technology, Nagaoka University of Technology, Niigata, Japan), Takayuki Abe, Mitsuhiro Inoue, Yuta Takahashi, Minoru Umeda

Oxidation and Reduction Selectivity at Pt-Ru-C Sputtered Electrodes in the Presence of Methanol and Oxygen

10:30 to 10:50 page 113

Xia Li (Department of Mechanical and Materials Engineering, University of Western Ontario, London, Canada), Mohammad Banis, Mei Cai, Xifei Li, Ruying Li, Jian Liu, Andy X. Sun, Biqiong Wang

Development of Doped and Coated Cathodes for Highly Stable Li-sulfur Batteries

10:50 to 11:10 page 190

Laurence Danis (Department of Chemistry, McGill University, Montreal, Canada), Janine Mauzeroll, Michael E. Snowden

Development of Nanoprobe for Localized Quantitative Detection of Mn^{2+} Produced at Battery Material

11:10 to 11:30 page 176

Vlastimil Vyskocil (Department of Analytical Chemistry, Charles University in Prague, Faculty of Science, Prague, Czech Republic), Zuzana Hrochová, Christian Iffelsberger, Zuzana Jurecková, Frank-Michael Matysik, Hana Smejkalová

Microcrystalline Natural Graphite–Polystyrene Composite Film – A Beneficial Electrode Interface for the Development of Electrochemical (Bio)Sensors

11:30 to 11:50 page 76

Winston Doherty (School of Applied Sciences and Engineering, Monash University, Gippsland Campus, Churchill, Australia), Samuel Adeloju

Fabrication of potentiometric penicillin G biosensor based on co-entrapment of penicillinase and MWCNTs within polypyrrole film

11:50 to 12:10 page 67

Aicheng Chen (Department of Chemistry, Lakehead University, Thunder Bay, Canada), Maduraiveeran Govindhan, Bal Ram Adhikari, Asieh Ahmadalinezhad, Sanghamitra Chatterjee, Badal Shah

Nanomaterials Based Electrochemical Biosensors for Medical Applications

Poster Presentations

Adsorption and charge transfer

s1-001

Lourdes Mónica Bravo Anaya (Ingeniería Química, Universidad de Guadalajara, Guadalajara, Mexico), M. Alejandra Álvarez Carreón, Víctor Vladimir Fernández, Jesús Gómez Gómez, Erika Roxana Larios Durán, Emma Rebeca Macías, J. Félix Armando Soltero

Impedance Transfer Function Designed to Simulate a Capacitive Behavior as a Function of Solute Concentration Evaluated for DNA-Au and DNA-Pt Interfaces

s1-002

Philipp Bron (Department of Chemistry, Philipps-Universtität Marburg, Marburg, Germany), Stefanie Dehnen, Sebastian Johansson, Bernhard Roling, Jörn Schmedt auf der Günne, Klaus Zick

$Li_{10}SnP_2S_{12}$: An Affordable Lithium Superionic Conductor

s1-003

Shannon Conlon (Department of Chemistry, University of Guelph, Guelph, Canada), Jacek Lipkowski, Ryan Seenath

An Investigation of the pH Dependent Barrier Properties of Scaffolded Vesicles

s1-004

Cheng-Yi Huang (Chemical and Materials Engineering, Chang Gung University, Taoyuan, Taiwan), Andrew S Lin

Study of the Electrochemical Oxidation of Dissolved Carbon Monoxide in Acidic and Alkaline Electrolytes by Using Au-RDE and Fabricated Au-Microelectrode

s1-005

Dorota Matyszewska (Faculty of Chemistry, University of Warsaw, Warsaw, Poland), Jan Biernat, Renata Bilewicz

Carbon Nanotubes Modified with Anticancer Drugs and Their Interactions with Model Membranes

s1-006

Sana Sabahat (Physics, COMSATS Institute of Information Technology, Islamabad, Pakistan), Zareen Akhter, Naveed Kausar Janjua

Electrochemical Investigation of Functionalized Gold Nanoparticles onto Electrode Surface

s1-007

Ulrich Stimming (Department of Physics E19, TUM CREATE & Technische Universität München, Garching, Germany), Rami Al-Oweini, Jochen Friedl, Max Herpich, Ulrich Kortz

Electrochemistry of tri-manganese substituted Keggin-ions

s1-008

YuYe J. Tong (Department of Chemistry, Georgetown University, Washington, USA), Thomas C. Allison, Yuan Gao, Ying Li, Georgeta C. Lica, Yangwei Liu

Charge Transfer through Metal Nanoparticle Thin Layers: Effect of Particle Size, Ligand Length, and Anchoring Element

Spectroelectrochemistry

s2-001

Przemyslaw Data (Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland), Alina Brzeczek, Mieczyslaw Lapkowski, Przemyslaw Ledwon, Krzysztof Walczak, Pawel Zassowski

Carbazole Based Star-Shaped Oligomers for Optoelectronics Applications

s2-002

Bhushan Gadgil (Laboratory of Materials Chemistry and Chemical Analysis, University of Turku, Turku, Finland)

Polythiophene derivative with pendant viologen side group: *In situ* ESR/UV-Vis-NIR spectroelectrochemical study

s2-003

Barbara Goodall (Department of Chemistry, University of Guelph, Guelph, Canada), Annia Kycia, Thamara Laredo, Jacek Lipkowski

Spectroscopic and Surface Analytical Studies of Gramicidin A in a Model Membrane

s2-004

Mieczyslaw Lapkowski (Faculty of Chemistry, Silesian University of Technology, Gliwice, Poland), Michal Czwartosz, Przemyslaw Data, Rafal Jedrysiak, Aleksandra Kurowska, Sandra Pluczyk, Pawel Zassowski

Diketopyrrole-pyrrole (DPP) derivatives: comparison of electrochemical and *in situ* spectroelectrochemical experiment with DFT simulations

s2-005

Piotr Pander (Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland), Przemyslaw Data, Katarzyna Laba, Mieczyslaw Lapkowski

Spectroelectrochemical and Electrochemical Properties of Novel Ruthenium Phthalocyanines Biaxially Ligated with Pyridine Derivatives

s2-006

Muzaffar Shodiev (Chemistry, University of Guelph, Guelph, Canada), Michael Grossutti, J. Jay Leitch, Jacek Lipkowski, Ryan Seenath

Determining the Structure and Orientation of the Alamethicin Ion Channel in the Opened and Closed States in Lipid Matrices using ATR and Electrochemical PMIRRAS

s2-007

Zhangfei Su (Department of Chemistry, University of Guelph, Guelph, Canada), Jacek Lipkowski, Adrian L. Schwan

Electrochemical and PM-IRRAS studies of valinomycin ionophores in a tethered bilayer lipid membrane

Advanced imaging techniques

s3-001

José Garcia-Anton (Ingeniería Quimica y Nuclear, Universidad Politecnica de Valencia, Valencia, Spain), Ramon Manuel Fernandez-Domene, Rita Sánchez-Tovar

Analysis of the Nanocurrents Generated on AISI 304 due to Pitting Corrosion by means of SECM

s3-002

Wojciech Nogala (Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland), Justyna Jedraszko, Martin Jönsson-Niedziolka, Magdalena Kominiak, Marcin Opallo

Preparation of SECM Nanoelectrodes Using Heating Coil Puller

Quantum chemical approaches and theoretical modeling

s4-001

Leandro Moreira de Campos Pinto (Institute of Theoretical Chemistry, Ulm University, Ulm, Germany), Wolfgang Schmickler

Some Catalytic Properties of Intermetallic Compounds

Organic and coordination electrochemistry

s5-001

Jessica Groppi (SBCS, Queen Mary University of London, London, United Kingdom), Philip Bartlett, Jeremy Kilburn

Toward the Control of Partial Covalent Modification of Glassy Carbon Surfaces Using Osmium Bipyridyl Complexes as Redox Centres

s5-002

Jiri Ludvik (Molecular Electrochemistry, J. Heyrovský Institute of Physical Chemistry, Prague 8, Czech Republic), Jiri Klima, Alan Liska

Electrochemical generation of stable oligo-radical anions of mono-, di-, tri- and tetranitrocalix[4]arenes

s5-003

Necati Menek (Department of Chemistry, Ondokuz Mayýs University, Sciences and Arts Faculty, Kurupelit Samsun, Turkey)

Investigation of Electrochemical Reaction Mechanism of Acýd Black 1 (C.I. 20470) By Using Voltammetric Techniques

s5-004

Guntars Vaivars (Department of Chemistry, University of Latvia, Riga, Latvia), Elina Ausekle, Anda Priksane, Aldis Zekunde

Impedance Analysis of Acidic Ionic Liquids

s5-005

Guntars Vaivars (Department of Chemistry, University of Latvia, Riga, Latvia), Janis Kleperis, Einars Sprugis

Composite SPEEK Polymer Membranes with Acidic Ionic Liquids

Electrochemical surface processes

s6-001

D. Abirami (Energetics Research Institute, Nanyang Technological University, Singapore), H.G. Ang, M.V. Sivaiah

Electrochemical Characterization of RuO_2 nanocomposite under Hydrogen Evolution Reaction

s6-002

Mona Amiri (Department of Chemistry, Lakehead University, Thunder Bay, Canada), Aicheng Chen, Maduraiveeran Govindhan

Effects of Temperature on Electrochemical Dissolution of Nickel in Ionic Liquids

s6-003

Habib Ashasisorkhabi (Physical Chemistry, University of Tabriz, Tabriz, Iran (Islamic Republic of))

A new process for direct *in situ* sonolectrochemical synthesis of PPy-Au nanocomposite coating and study of its corrosion protection performance

s6-004

Gunars Bajars (Department of Semiconducting Materials, University of Latvia, Riga, Latvia), Liga Grinberga, Janis Kleperis, Ineta Liepina, Andris Sutka, Martins Vanags

Photocatalytic Activity of Ferrite Based Nanoparticles, Their Clusters and Thin Films for Solar Water Splitting

s6-005

Gunars Bajars (Department of Semiconducting Materials, Institute of Solid State Physics, University of Latvia, Riga, Latvia), Karina Bikova, Janis Kleperis, Gints Kucinskis, Andrejs Lusis

Studies of $LiFePO_4$ Cathode – Electrolyte Interface

s6-006

Zaira Bedolla (Nanostructures, Universidad Nacional Autónoma de Mexico, Ensenada, Mexico), Gabriel Alonso, Yadira Gochi, Ysmael Verde

Methanol oxidation on Pt/CNT electrocatalysts promoted with TiO_2

s6-007

Xin Chang (Department of Chemistry, Lakehead University, Thunder Bay, Canada), Aicheng Chen, Sapanbir S. Thind, Jiali Wen

Significant Enhancement in the Electrochemical Catalytic Activity of Titanium Dioxide Nanotubes

s6-008

Ling Chen (College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China), Shi-Gang Sun, Chang-Deng Xu, Jin-Yu Ye, Chun-Hua Zhen

Study of Interaction of CTAB with Au Single Crystal Electrodes Towards Understanding the Role of CTAB in Shape-Controlled Synthesis of Nanomaterials

s6-009

Nico Cousens (Chemistry, University of Oxford, Oxford, United Kingdom), Judy Britton, Nicole Grobert, Susan Perkin

The Electrochemical Graphene Surface Force Balance

s6-010

Shengyuan Deng (School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing, China), Baojing Zhou

G-Quadruplex Promoted Electrogenerated Phosphorescence of Zinc(II) Protoporphyrin IX as DNAzyme for Molecular-Scale Signal Transduction

s6-011

José Garcia-Anton (Ingeniería Quimica y Nuclear, Universidad Politecnica de Valencia, Valencia, Spain), Kiyoung Lee, Rita Sánchez-Tovar, Patrik Schmuki

Anodic Nanoesponges Formation in the Hydrodynamic Anodization of TiO_2

s6-012

Rosa Gonzalez (Departamento de Ingeniería Química, IPN-ESIQIE, México D.F., Mexico), Sarahi Pacheco, Roberto Vargas

Synthesis and characterization of Pt/CeO_2 NT electrocatalyst for the oxygen reduction reaction

s6-013

Virginija Kepeniene (Department of Catalysis, Center for Physical Sciences and Technology, Vilnius, Lithuania), Rokas Kondrotas, Eugenijus Norkus, Vidas Pakštas, Loreta Tamašauskaite-Tamašiunaite, Jürate Vaiciüniene

Dependence of Platinum-Niobium Oxide/C Catalysts Activity on the Conditions of Preparation of Primary Niobium Oxide/C Composites

s6-014

Saghar Khoshmashrab (Department of Chemistry, The University of Western Ontario, London, Canada)

Characterization of Cu_2ZnSnS_4 Nanocrystal Thin Films for Solar cells

s6-015

Veniamin Kondratiev (Chemical Department, St.Petersburg State University, St.Petersburg, Russia), Svetlana Eliseeva, Alexandra Nizhegorodova

Synthesis and Electrochemical Study of Nanostructured PEDOT/MnO_2 Composites for Supercapacitor Applications

s6-016

Joo-Yul Lee (Electrochemistry Lab, Korea Institute of Materials Science, Changwon , Korea), Yongsoo Jeong

Fabrication of Micro Probe Pin through Electrolytic and Electroless Ni Alloy Deposition

s6-017

Haijin Liu (Department of Chemistry, Lakehead University, Thunder Bay, Canada), Aicheng Chen, Sapanbir Thind, Jiali Wen, Guosheng Wu

Synthesis of N, Zr Co-doped Mesoporous TiO_2 with Enhanced Photocurrent and Photocatalytic Activity

s6-018

Andrew Morrison (Department of Chemistry, University of Guelph, Guelph, Canada), Jacek Lipkowski, Md Golam Moula

Anodic Dissolution of Vapor Deposited Nickel: Investigation of Residue Formation

s6-019

Md Golam Moula (Department of Chemistry, University of Guelph, Guelph, Canada), Henry Huang, Jacek Lipkowski

Relation Between the Electrochemical Dissolution and Surface Morphology of Vapor Deposited Nickel

s6-020

Martin Opitz (Department of Chemistry, University of Marburg, Marburg, Germany), Joachim F. Beleites, Bernhard Roling, Bernd Smarsly, Junpei Yue

Titanium Oxide-based Nanocrystalline Materials for Pseudocapacitors

s6-021

Piotr Ozga (Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Kraków, Poland), Honorata Kazimierczak, Monika Slupska

Characterization and Modification of Surface Topography During Electrodeposition of Tin and Zinc Based Alloys from Citrate Complex Baths

s6-022

Valentín Pérez-Herranz (Ingeniería Química y Nuclear, Universitat Politècnica de València, Valencia, Spain), Graciela González, Cristina González-Buch, Emma M. Ortega, Ignacio Pedre, Guadalupe Sánchez-Loredo

Activation of Macroporous Ni electrodes with Ag and AgS Nanoparticles for Hydrogen Production

s6-023

MinHo Seo (Department of Chemical Engineering, University of Waterloo, Waterloo, Canada), Zhongwei Chen, Drew Higgins, Hey Woong Park

The *ab-initio* study of iron phtalocyanie derived Fe-SPc catalysts for oxygen reduction reaction (ORR) in PEM Fuel Cells

s6-024

Scott R. Smith (Department of Chemistry, University of Guelph, Guelph, Canada), Janet Y. Baron, Yeonuk Choi, Yi-Fan Huang, Song-Bo Li, Jacek Lipkowski, Xiang-Dong Tian, Zhong-Qun Tian

Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy Investigations of Thiosulfate Gold Leaching

s6-025

M.E. Snowden (Department of Chemistry, McGill University, Montreal, Canada), S. Gervais, Janine Mauzeroll, S.B. Schougaard

Localized Investigations of the Electrochemical Properties of Lithium Iron Phosphate Films using Micro-Pipets

s6-026

Camillo Spöri (Institut für Chemie, Technische Universtität Berlin, Berlin, Germany), Peter Strasser, David P. Wilkinson

Comparative exploration of the surface electrochemistry of Ir-IrO_2 (111 / 110) and Ru-RuO_2 (0001) single crystal model catalysts for the oxygen evolution reaction (OER)

s6-027

Daniel Stitt (Chemistry, The University of Western Ontario, London, Canada), Zhifeng Ding

Selenization of CuInS2 Nanocrystal Films: Controlling Dropcasting Uniformity by Post-Synthesis Addition of PVP

s6-028

Essen Suleimenov (Laboratory of Advanced Materials and Technology, Kazakh British Technical University, Almaty, Kazakhstan)

Decomposition Aluminate Solutions from the Electrochemical Reaction with Metallic Aluminum

s6-029

Amy Tapley (Chemistry, Western University, London, Canada), Zhifeng Ding, David Love

Characterization and Optimization of $CuInS_2$ as a Light Absorbing Layer for Solar Cells

s6-030

Hanna Trzeciakiewicz (Chemistry, Oakland University, Washington, USA), Sanela Martic

Electrochemical behavior of Tau protein domain on binding to aggregation agent

s6-031

Matthew Turnbull (Chemistry, Western University, London, Canada), Zhifeng Ding

PECM Study of Post-Synthesis PVP Addition and Selenization as a Method for Improving CZTS Films

s6-032

Jens Wallauer (Department of Chemistry, Philipps-University Marburg, Marburg, Germany), Marcel Drüschler, Bernhard Roling

Fast and slow processes at the interface between ionic liquids and Au(111)-electrodes

s6-033

Chunqing Zhou (Department of Chemistry, University of Guelph, Guelph, Canada), Yeonuk Choi, Jacek Lipkowski, Scott Smith

ElectroChemical Studies of Gold Leaching in Thiosulfate Solution with Copper

Modern applications of interfacial electrochemistry

s7-001

Mahdieh Atighilorestani (Chemistry, University of Victoria, Victoria, Canada)

Electrochemical Response from Cylindrical Nanopore Electrode Arrays

s7-002

Walaa Alammari (Department of Chemistry, Lakehead University, Thunder Bay, Canada), Aicheng Chen, Kevin Gagnon

Electrocatalytic Activity of PtIr and PtRu Nanoparticles Deposited on TiO_2 Nanotubes

s7-003

Marco Balabajew (Chemistry, Philipps-Universitaet, Marburg, Germany), Bernhard Roling

An Electrochemical Impedance Spectroscopy Study of Anion Intercalation in Dual-ion Cells

s7-004

Han-Yi Chen (School of Materials Science and Engineering, TUM CREATE and Nanyang Technological University, Singapore, Singapore)

Polyoxometalates as Electrode Materials for Molecular Cluster Batteries

s7-005

Hiroshi Fukunaga (Faculty of Textile Science and Technology, Shinshu University, Ueda City, Japan), Jin Fukaya, Yoshiyuki Hattori, Iori Shimada, Nobuhide Takahashi, Toru Takatsuka

Effect of Surface Area on Oxygen Reduction Reaction of Silk-Derived Activated Carbon as PEFC Cathode

s7-006

Michael Gellert (Physical Chemistry, Philipps-Universitaet Marburg, Marburg, Germany), Katharina Ines Gries, Bernhard Roling, Fabio Rosciano, Stefan Spannenberger, Kerstin Volz, Chihiro Yada, Julia Zakel

$LiNi_{0.5}Mn_{1.5}O_4$ Thin-Film Cathodes on Gold-Coated Stainless Steel Substrates: Structural and Electrochemical Properties

s7-007

Mohammadreza Ghavidel (Faculty of Science, Chemistry, University of Ontario, Institute of Technology, Oshawa, Canada), E. Bradley Easton

Effects of metal loading on the structure and activity of Pt-Mn alloys towards ethanol oxidation

s7-008

Vinci Hung (Physical and Environmental Sciences, University of Toronto Scarborough, Toronto, Canada), Kagan Kerman

Electrochemical Detection of Caspase-3 Activity

s7-009

Thomas Jaensch (Department of Chemistry, University of Marburg, Marburg, Germany), Bernhard Roling

Hierarchically Structured Carbide-Derived Carbons and Ionic Liquids as Improved Materials for Supercapacitors?

s7-010

Wei Jin (Chemistry, Lakehead University, Thunder Bay, Canada), Aicheng Chen, Rasha Tolba, Jiali Wen, Guosheng Wu

Novel Electrochemical Extraction of Lignin from Black Liquor and Its Application for the Removal of Cr(VI)

s7-011

Tetsuro Kobayashi (Battery Lab., Toyota Central R&D Labs., Inc., Nagakute, Japan), Yasuhito Kondo, Hidehito Matsuo, Takamasa Nonaka, Hiroshi Nozaski, Yoshio Ukyo, Satoshi Yamaguchi

Extensive Study on the Redox Mechanism of Nickel Hydroxide II; Inhomogeneous Reaction in Nickel Hydroxide Particle

s7-012

Xiao Lin (School of Chemistry and Chemical Engineering, Queens University Belfast, Belfast, United Kingdom), Zhao-Yang Chen, You-Qun Chu, Christopher Hardacre, Jia-mei Jin, Wen-Feng Lin, Chun-An Ma

Synthesis, Structure and Reactivity of WC@meso-Pt Core-Shell Nano-Electrocatalyst for Fuel Cells

s7-013

Wenjuan Liu (R&D and IP, Microvast Inc., Stafford, USA)

The Development and Perspectives of Advanced Batteries

s7-014

Jan Macak (Department of General and Inorganic Chemistry, University of Pardubice, Pardubice, Czech Republic), Tomas Kohoutek, Jakub Kolar, Tomas Wagner

Towards functional advanced materials using ordered anodic oxides supports and templates

s7-015

Samantha Matthews (Department of Chemistry, State University of New York at Potsdam, Potsdam, USA), Maria Hepel, Ondrey Kubesa, Kathleen Morrisey

Novel Biosensors for Determination of Phenolic Compounds using Catalyst-Loaded Reduced Graphene Oxide Substrates

s7-016

Edyta Matysiak (Faculty of Chemistry, Warsaw, Poland), Anna Nowicka

Sensitive Detection of Hemoglobin with Electrodes Modified with Magnetic Nanoparticles

s7-017

Amin Nouri-Khorasani (Chemical and Biological Engineering, The University of British Columbia, Vancouver, Canada), David P. Wilkinson

Effect of Nanoscale Catalyst Structure on the Mass Transport Properties in Cathode Catalyst Layers of PEM Fuel Cells

s7-018

Maxim Smetanin (Chemistry Department, University of Guelph, Guelph, Canada), Jacek Lipkowski, Flavio Maran

Aggregation of Trichogin in a Lipid Monolayer Deposited at the Au(111)Electrode Surface

s7-019

Biqiong Wang (Mechanical and Materials Engineering, University of Western Ontario, London, Canada), Mohammad Banis, Mei Cai, Yuhai Hu, Xifei Li, Ruying Li, Jian Liu, Tsunkong Sham, Andy X. Sun, Biwei Xiao

Free-Standing Paper-Based Nano-Carbon Composites as Binder-Free Anode for Lithium Ion Batteries

s7-020

Biwei Xiao (Department of Mechanical and Materials Engineering, University of Western Ontario, London, Canada), Craig Langford, Xifei Li, Xia Li, Ruying Li, Andy X. Sun, Biqiong Wang

Graphene Nanoribbons Derived from the Unzipping of Carbon Nanotubes: Controlled Synthesis and Superior Lithium Storage Performance

s7-021

Hossein Yadegari (Department of Mechanical and Materials Engineering, University of Western Ontario, London, Canada), Yongliang Li, Ruying Li, Xueliang Sun

Nanostructured Carbon Based Electrode Materials for Rechargeable Li- and Na-Air Batteries

s7-022

Zhaoyang Zhang (Department of Chemistry, Lakehead University, Thunder Bay, Canada), Aicheng Chen, Daniel Liba

Continuous Separation and Recovery of Cr(III) and Cr(VI) Using Electrodeionization

Abstracts of Keynote lectures, Invited Oral presentations, Oral presentations and Poster presentations

Modification of electrodes by electrochemical reduction of diazonium ions

Daniel Bélanger
Département de Chimie, Université du Québec à Montréal, CP 8888, succ. Centre-Ville
Montréal (Québec), Canada, H3C 3P8
belanger.daniel@uqam.ca

The modification of carbon, semiconductor, metallic and metal oxide surfaces by electrochemical and spontaneous reduction of aryldiazonium salts has been widely investigated by several research groups in the past two decades since the pioneering work of Pinson and coworkers (Bélanger and Pinson, Chem. Soc. Rev. 2011, 40, 3995). It is now well known that the electrochemical reduction of diazonium salts leads to the covalent attachment of aryl groups onto a variety of substrates including solid electrodes and powders. Modification based on in-situ generated diazonium cations has proved to be very convenient and is now widely used. This electrografting process can be carried out in various conditions that include acidic, neutral and alkaline aqueous media, non-aqueous electrolyte, room temperature ionic liquid and even with pure diazonium salt alone. In this talk, recent results from our laboratory will be presented and discussed.

Building a Biomimetic Membrane at an Electrode Surface

J.Lipkowski
Department of Chemistry, University of Guelph, Guelph,Ontario, N1G 2W1
Canada
jlipkows@uoguelph.ca

I will describe several years of our efforts to build a model biological membrane at a surface of a gold electrode. In this architecture, the membrane may be exposed to static electric fields on the order of 10^7 to 10^8V/m. These fields are comparable in magnitude to the static electric field acting on a natural biological membrane. The field may be conveniently used to manipulate organic molecules within the membrane. By turning a knob on the control instrument one can force phase transitions in the film of organic molecules or force them to disperse or to aggregate at the surface. We use electrochemical techniques to control the physical state of the film while the photon polarization infrared reflection absorption spectroscopy (PMIRRAS), surface imaging by STM and AFM and neutron scattering techniques are employed to study conformational changes of organic molecules and their ordering within the membrane. I will show examples of a membrane build of a simple zwitterionic phospholipid such as DMPC and a mixed membrane composed of DMPC and cholesterol. Our results will illustrate a tremendous effect of cholesterol on the membrane structure. I will also compare two methods of membrane deposition at the electrode surface, namely by unilamellar vesicles fusion and using the Langmuir-Blodgett technique. Applications of these model systems to study interactions of small antibiotic peptides with lipids are discussed. I will also describe our efforts to build a floating bilayer in which the model membrane is separated from the metal by a water rich region.

Water and Ions at the Electrochemical Interface Studied by Surface-Enhanced Infrared Absorption Spectroscopy

Akira Yamakata,[1] Kenta Motobayashi,[2] Takaya Ishino,[2] Akihiro Morita,[3] and Masatoshi Osawa*[2]
[1]Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan
[2]Catalysis Research Center, Hokkaido University, 001-0021, Japan
[3]Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

Electric double layer at the electrode/aqueous solution interface is composed of water molecules, specifically adsorbed anions, and hydrated cations. Surface-enhanced infrared absorption spectroscopy (SEIRAS) is one of the useful techniques to investigate the electric double layer owing to its high sensitivity and interface selectivity. [1] SEIRAS has revealed that interfacial water changes its orientation depending on the applied potential.[2] Specific adsorption of anions on electrodes also has been well studied by SEIRAS and other vibrational spectroscopy techniques. Compared with water and anions, studied on the behavior of cations are limited. This presentation will focus on dynamic behaviors of water and cations, including tetraalkylannmonium (RN_4N^+; R=ethyl, propyl, and Bu) and alkaline metals, on a CO-covered Pt surface against external perturbations (potential and temperature).[3,4] This system serves as a model for understanding hydrophilic and hydrophobic interactions of chemical substance in aqueous solutions. Nanosecond time-resolved measurements and molecular dynamics simulation reveal that hydrated cations are concentrated at the interface and their hydration shells are collapsed when the electrode surface is negatively charged on a time scale of ms. Additionally, the electric double layer at the electrode and ionic liquid interface will be discussed. Strong coulomb interactions among ions and the surface lead to a hysteresis in the potential-induced restructuring of the double layer.[5]

Reference
[1] M. Osawa, *Bull. Chem. Soc. Jpn.*, **70**, 2861 (1997)
[2] M. Osawa et al. *J. Phys. Chem. C*, **112,** 4248 (2008).
[3] A. Yamakata and M. Osawa, *J. Am. Chem. Soc.*, **131**, 6892 (2009).
[4] A. Yamakata et al, *J. Am. Chem. Soc.*, **135**, 15033 (2013)
[5] K. Motobayashi et al., *J. Phys. Chem. Lett.*, **4**, 3110-3114 (2013).

Plasmonic-Based Electrochemical Current and Impedance Imaging

NJ Tao
Center for Bioelectronics and Biosensors, Biodesign Institute
School of Electrical, Computer and Energy Engineering
Tempe, AZ85287
njtao@asu.edu

Continued advances in life sciences and biotechnologies require new sensing and imaging capabilities. An important and widely used sensing method is electrochemical detection, which is based on detecting an electrochemical current or related quantity by applying a potential to an electrode. Another method is electrochemical impedance spectroscopy for label-free analysis of biomolecules. These methods have been used for a wide range of applications, including chemical analysis, glucose and neurotransmitter monitoring, DNA and protein detections, and electrocatalysis studies, but they do not provide local reaction information. Such information is critical for many applications, such as heterogeneous reactions, local activities of cells, and high-throughput protein and DNA microarrays.

We have developed a technique to image local electrochemical current and impedance without using a scanning probe or a microelectrode. Instead of measuring the current with an electrode, we determine the electrochemical current density from an optical signal generated from a surface plasmon resonance (SPR). Important benefits of this approach include fast and non-invasive electrochemical current and impedance imaging of the surface. In addition, the measured local current signal is proportional to the incident light intensity, which does not scale with the area of a region of interest, allowing for high spatial resolution without sacrificing current detection limit. Using the techniques, we have demonstrated various applications, including sensitive and selective trace analysis, protein microarrays, and single cell studies.

Oral presentation

Self-discharge in Manganese Oxide Electrodes for Neutral-Aqueous-Electrochemical Capacitors

Heather A. Andreas
Department of Chemistry, Dalhousie University
Halifax, NS, B3H 4R2
heather.andreas@dal.ca

Manganese oxide electrodes are gaining popularity in research circles for use in electrochemical capacitors with a neutral Na_2SO_4 electrolyte. This gain in popularity is due in large part to the fact that manganese oxide is pseudocapacitive, like ruthenium oxide, but significantly less expensive. Of course, as with all electrochemical capacitors, manganese oxide electrodes undergo self-discharge. Unlike many materials, however, the self-discharge of manganese oxide electrodes in 0.5 M Na_2SO_4 has not been extensively studied.

The self-discharge profile of manganese oxide (Figure 1) has a complicated structure indicating multiple self-discharge processes. The initial linear drop in potential with log time signifies the presence of a Faradaic reaction, the identity of which will be discussed in this presentation. The Faradaic reaction discharges the surface of the manganese oxide resulting in charge redistribution through the oxide film. Since the pseudocapacitive reactions of manganese oxide are confined to the surface of the material, it was expected that the charge redistribution in would occur with charge moving from the electrode surface to the bulk. In fact, the self-discharge profile, in particular the slowing of the self-discharge at potentials near 0.68 V, indicate charge movement from the bulk to the surface of the film.

This presentation will elucidate the self-discharge process occurring in this films and methods to minimize this self-discharge in electrochemical capacitors of these materials.

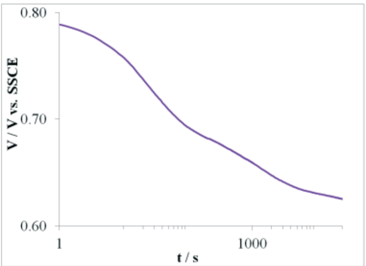


Figure 1 - Self-discharge of electrodeposited manganese oxide on stainless steel in 0.5 M Na_2SO_4, plotted as a function of log time.

Surface Immobilisation of Nanostructured Polyoxometalates and their Electrocatalytic Applications

Nargis Anwar, Timothy McCormac
Electrochemistry Research Group, DkIT Dundalk. County Louth, Ireland
nargis.anwar@dkit.ie

Polyoxometalates (POMs) are a large, incredibly varied family of metal oxide clusters based on the early transition metals V, Mo and W in high oxidation states, with an almost unmatched range of structural types and physical properties. Surface immobilised POMs are being used in a variety of important fields as catalysis[1], sensors[2] nanotechnology[2] and electronics[2]. In this work two techniques are employed to immobilise the POMs. The well known conducting polymer, Poly-3,4-Ethylenedioxythiophene (PEDOT) was used for the immobilisation of the $Na_9(NH_4)_5[\{(\beta\text{-}\alpha\text{-}PW_9O_{34})Co_3(OH)(H_2O)_2(Ale)\}_2Co]\cdot 35H_2O$ $[Co_7(Ale)_2]$ onto glassy carbon electrode surfaces. Electrochemical investigations yielded stable and well behaved films. These films, of varying thickness, were stable in within the pH domain 6-10 and electrochemical redox processes associated with both the incorporated POM and polymer itself were clearly observed. Organised multilayer assemblies were constructed using the well known Layer by layer technique (LBL) through alternating anionic POM$[Co_7(Ale)_2]$, layers and the cationic, Methylene blue (MB), with PDDA [poly(diallyldimethylammonium chloride)] used as a base cationic polymer layer. Stable redox couples associated with the W-O framework and Co-redox couple were clearly observed upon redox switching within the pH 6. The constructed multilayer assembly showed good stability towards redox cycling. The porosity and permeability of the multilayer assembly towards anionic and cationic probes was determined. Further investigations into the multilayer assembly were undertaken by determining the charge transfer resistance and heterogeneous rate constant, using AC-impedance and Cyclic voltammetry respectively. The layer also showed catalytic ability towards the reduction of H_2O_2.

References:

[1] S. Dong, M. Liu. *Electrochim. Acta*. 39 (1994) 947.
[2] M.T.Pope., A., Muller; *Polyoxometalates Chemistry: From Topology via Self Assembly to Applicaations*; Eds. Kluwer Dordrecht, The Netherlands, **2001**

Electrochemical Impedance Spectroscopy Investigation of Microstructural Effects on the Corrosion of Mg Alloys

R. Matthew Asmussen, W. Jeff Binns, Pellumb Jakupi, David Shoesmith*
Department of Chemistry and Surface Science Western, University of Western Ontario
1161 Richmond St, London, ON, Canada
dwshoesm@uwo.ca

Mg alloys are likely to be crucial components of fuel-efficient vehicles due to their low cost and high strength to weight ratio. Due to galvanic corrosion resulting not only from coupling to other structural materials but also micro-galvanic coupling between the Mg matrix and secondary microstructures in the alloy, their current usage is limited. We have been investigating microgalvanic corrosion processes using a combination of surface analyses (scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM)) and electrochemical experiments, in particular electrochemical impedance spectroscopy (EIS). Three casts of the AM50 Mg alloy (sand, graphite and die cast) have been investigated in a saline environment. Alteration of the casting process changes only the size and distribution of the secondary phases in the α-Mg matrix not the alloy composition. The secondary phases become less widely distributed in the order sand > graphite > die. Electrochemical measurements (corrosion potential, potentiodynamic polarization,) show the die cast alloy possesses the highest corrosion resistance. Corrosion damage on the sand and graphite cast alloys accumulates preferentially on α-grains with a low Al-content surrounded by a skeletal corrosion resistant region containing higher Al. By contrast the die cast alloy exhibits much more variance in corrosion behaviour and the location of corrosion damage.

These differences in corrosion resistance and damage morphology with changing microstructure can also be seen in EIS measurements. In 1.6 wt% NaCl, the sand and graphite cast alloys exhibit a single time constant, with the graphite cast having a slightly larger overall impedance, while the die cast alloy displays two time constants. The distinct EIS behaviour of the die cast alloy can be attributed to its more heterogeneous composition, which results in the formation of an oxide/hydroxide bilayer on the alloy surface. The sand and graphite casts with their lower corrosion resistance, undergo major corrosion events which dominate the EIS response. When the chloride concentration is reduced, EIS indicates a general increase in impedance on the alloy surfaces, and two time constants develop for all alloys, the initiation of major corrosion events being reduced.

Specific adsorption of perchlorate anions and Nafion® on Pt{hkl}: their influence on the Oxygen Reduction Reaction

Gary A. Attard, Ashley Brew, Katherine Hunter, Jonathan Sharman* and Edward* Wright
School of Chemistry
Cardiff University, Park Place
Cardiff CF10 3AT, UK
attard@cardiff.ac.uk

In a recent publication, Omura *et al.*[1] demonstrated that perchlorate anions are specifically adsorbed at polycrystalline Pt electrocatalysts in aqueous acidic media and that such behavior caused a decrease in the activity of the electrocatalyst towards the oxygen reduction reaction. We have extended these investigations of perchlorate anion specific adsorption under acidic conditions to include platinum single crystal electrode surfaces since the voltammetric response of such surfaces is known to be profoundly influenced by the nature of the electrosorbing anion. For all surfaces studied, specific adsorption of perchlorate was confirmed. Furthermore, inhibition of oxygen reduction reaction (ORR) activity was observed for the highest perchlorate concentrations studied. Comparison of perchlorate anion specific adsorption strength and that of sulphonate moieties contained within a Nafion® - modified Pt{hkl} electrode will also be discussed.

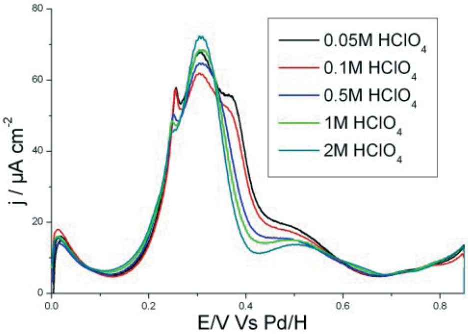


Figure 1. CV of Pt{100}- (1x1) in perchloric acid. Sweep rate = 50 mV/s.

[1] J. Omura, H. Yano, M. Watanabe and H. Uchida, *Langmuir*, **27** (2011) 6464.

*Johnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading, RG4 9NH, UK

Oral presentation

DEMS study: Ethanol and acetaldehyde stripping on Pt/C electrocatalyst at room temperature

A. Bach Delpeuch, C. Cremers, M. Chatenet, J. Tübke
Fraunhofer Institut für chemische Technologie ICT
Joseph-von-Fraunhofer-Straße 7, 76327 Pfinztal, Germany
Antoine.bach.delpeuch@ict.fraunhofer.de

The direct ethanol fuel cell (DEFC) may be a good candidate for future commercialized power sources thanks *inter alia* to its high energy density. However DEFC performances still remain theoretical notably due to the difficulty to break the C-C bond during the ethanol electrooxidation reaction. As a consequence, the molecule can not completely oxidize to CO_2 ($12e^-$) which hinders dramatically the DEFC performances. One main product of the ethanol oxidation is acetaldehyde which only corresponds to the ethanol dehydrogenation process ($2e^-$).

Further information on the mechanism of the ethanol oxidation and particularly on the C-C bond cleavage could help solve this issue. A deeper insight in the EOR mechanism could be achieved in studying the formation and oxidation of the adsorbed reaction intermediates. To that extent, stripping of ethanol and of ethanol electrooxidation intermediates, such as acetaldehyde, on platinum electrocatalysts could be performed.

Ethanol and acetaldehyde strippings on 20 wt.% Pt/C synthesized by a polyol method was investigated in acidic medium at room temperature using online differential electrochemical mass spectrometry (DEMS). The variation of the adsorption potential is studied. A quantified analysis of the adsorbates distribution on the electrocatalyst surface for both ethanol and acetaldehyde stripping was performed.

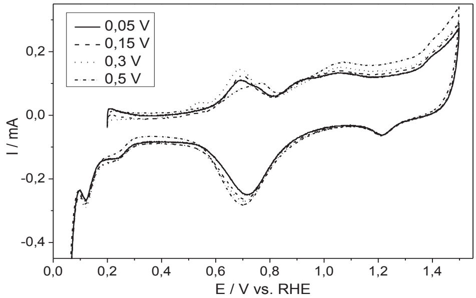


Fig. Ethanol stripping cyclic voltammetries in 0.5 M H_2SO_4 on Pt/C after ethanol adsorption in 0.5 M H_2SO_4 +0.1 M EtOH for 500 s; v = 10 mV s^{-1}, T = 25°C.

Molecularly Imprinted Polymer Grafts Through Interfacial Chemistry Of Aryl Diazonium Salts For Highly Selective And Sensitive Electrochemical Sensors

Idriss Bakas* and Mohamed M. Chehimi*
Univ Paris Diderot, ITODYS, CNRS, 15 rue J-A de Baïf, 75013 Paris, France
(Idrissbakas@gmail.com ; chehimi@univ-paris-diderot.fr)

Molecular imprinting is a technique for preparing polymers with desired and predetermined selectivity. Functional groups of template molecules (for which selectivity is desired) are used to create interactions with monomer(s) prior to polymerization process. Template molecules are extracted after polymerization, leaving well-defined, 3D cavities with spatially oriented functionalities in the highly cross-linked polymer. In order to design MIP-based electrochemical sensors, it is convenient to synthesize MIP films via electrode surface-initiated polymerization. The MIP layers are particularly interesting because they are easy and fast to prepare, low cost, and ensure pico- to nanomolar detection limits.

Herewith, we describe the preparation of MIPs by surface-initiated photopolymerization on electrodes grafted with initiators such as N,N-dimethylaminophenyl or 4-benzoyl phenyl groups from the electroreduction of their parent aryl diazonium salts. Copolymerization of methacrylic acid (functional monomer, F), and ethylene glycol dimethacrylate (cross-linker, C) was conducted in porogenic solvents (e.g. DMSO) and in the presence of template molecules (T) such as melamine (Fig. 1). Near picomolar limit of detection can be achieved by controlling: (i) MIP formulation (T/F/C molar ratio), (ii) nature of porogenic solvent, (iii) rebinding solvent, (iv) pH of solution, (v) ionic strength, (vi) embedding gold nanoparticles in the MIP layers. It is noteworthy that MIP layers are highly selective and sensitive; can be adapted to different electrode materials and arrays, and used for molecular recognition in complex matrices (e.g. milk).

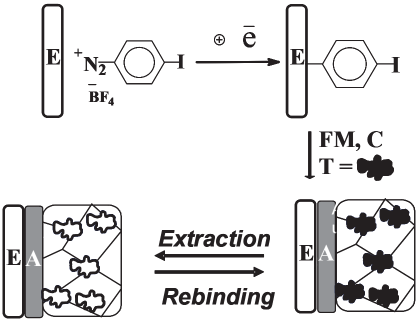


Fig. 1. Making MIP grafts on electrodes (E). I: initiator, FM: functional monomer, C: crosslinker, T: template molecule, A: aryl layer.

Ammonia electrooxidation on bimetallic PtIr and NiPd nanoparticles in alkaline media

Elena A. Baranova, Anis Allagui, Saad Sarfraz, Spyridon Ntais
Department of Chemical & Biological Engineering, Centre for Catalysis Research and Innovation (CCRI) University of Ottawa, 161 Louis-Pasteur
Ottawa ON K1N 6N5 Canada
elena.baranova@uottawa.ca

Recent developments of alkaline anion-exchange membranes that conduct hydroxyl (OH^-) ions opened up the way for further advance of direct alkaline fuel cells. Electrocatalysis of oxidation reactions is facilitated in alkaline electrolytes; while it is promising from an economical point of view, because of the potential use of more abundant and non precious catalysts. One of the potential fuels for the direct alkaline fuel cells is ammonia because the theoretical specific charge of complete ammonia oxidation to N_2 is 4.75 A h g^{-1} which is 95% of the charge of methanol oxidation to CO_2 [1]. Moreover, anhydrous liquid ammonia is a compact hydrogen carrier. Its specific volume of hydrogen content is higher by 70% than liquid hydrogen showing 50% increase of specific energy density. Another advantage of liquid ammonia is that it can be used as a distribution and storage medium [2]. However, the slow kinetics of this process at low temperatures imposes the use of efficient electrocatalysts in order to oxidize ammonia to N_2 at reasonable rates.

The present work aims at the investigation of electrooxidation of ammonia on PtIr and Ni_xPd_{1-x} nanoparticles. To this end, PtIr (70:30 at. %) and NiPd (99 : 1; 95 : 5 and 50:50 at. %) nanoparticles were synthesized using the modified polyol method and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) [3,4]. Electrocatalytic activities of NiPd and PtIr were studied in 1 M KOH using cyclic voltammetry and chronoamperometry techniques. Electrolysis under galvanostatic conditions was used to investigate the products of ammonia oxidation by standard titration methods. Furthermore, detailed XPS was used to investigate the surface composition and the electronic effect in bimetallic nanoparticles. The detailed investigation of electrochemical behaviour of ammoniaon bimetallic nanoparticles will be discussed and correlated to their physicochemical properties.

1. G. Strickland, Int J Hydrogen Energy (1984) 9(9):759-66.
2. E.L. Simons, E.J. Cairns, D.J. Surd, J Electrochem Soc(1969)116(5):556-61.
3. A. Allagui, S. Sarfraz, E.A. Baranova, Electrochim Acta (2013),110, 253-259.
4. A. Allagui, M. Oudah, X. Tuaev, S. Ntais, F. Almomani, E.A. Baranova, Int J Hydrogen Energy (2013) 38, 2455-2463.

Plasmonic Electrode Structures for Electrochemical SERS

Philip N. Bartlett
University of Southampton
Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ (UK)
pnb@soton.ac.uk

Using electroplating through self-assembled templates formed from close packed arrays of uniform colloidal particles it is possible to simply and predictably control the geometry of the nanostructured films produced.

Using templates with diameters between 450 and 1200 nm we can produce surfaces that show significant enhancement in surface enhanced Raman spectroscopy (SERS). We have investigated the origins of this surface enhancement by varying the film thickness, template sphere diameter and by looking at the angular dependence. The intensity of the SER spectra varies with all of these factors indicating that the precise geometry of the structured surface and the excitation of surface plasmons is important [1]. These surfaces can be used for practical applications in SERS, for example in *in situ* electrochemical studies [2] or for discrimination of DNA [3] and to study the mechanisms of the SERS process [4].

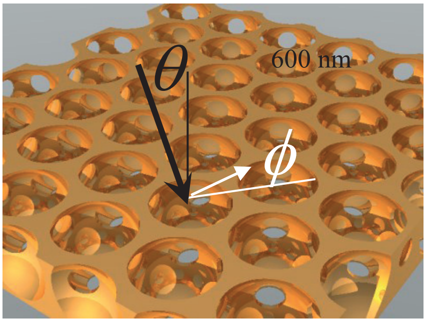


Fig 1 Schematic of a sphere segment void surface

References

[1] P. N. Bartlett *et al*., *Faraday Discuss*. 2004, **125**, 117; T. A. Kelf *et al*., *Phys. Rev. B*, 2006, **74**, Art. No. 245415.

[2] M. Abdelsalam *et al.*, *Langmuir* 2008, **24**, 7018.

[3] R. P. Johnson *et al., J. Am. Chem. Soc*., 2012, **134**, 14099; R. P. Johnson *et al.*, *Langmuir*, 2012, **28**, 5464; R. P. Johnson *et al.*, *Chem. Sci*., 2013, **4**, 1625.

[4] S. Mahajan *et al*., *J. Phys Chem., C* 2009, **113**, 9284; S. Mahajan *et al.*, *J. Phys. Chem. C* 2010, **114**, 7242; J. D. Speed *et al*., *Chem. Commun*. 2011, **47**, 6335; R. P. Johnson *et al.*, *Phys. Chem. Chem. Phys*. 2011, **13**, 16661.

Ordering of 2-Octadecanoylaminoacetic Acid at Air-Water and Solution-Au(111) Interfaces

Renata Bilewicz[1], Jan Pawlowski[2], Dorota Matyszewska[2], Elzbieta Jablonowska[1], Slawomir Sek[2], Ehud Landau[3]
[1]*Faculty of Chemistry, University of Warsaw, Pasteura ,1 Poland,*
[2]*Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland.*
[3]*Institute of Organic Chemistry, University of Zurich, Switzerland*

Adsorption of 2-octadecanoylaminoacetic acid and of its bulky headgroup neutral derivative on three different substrated are described. The formation of layers by the Langmuir-Blodgett technique at the air-water interface was monitored at pure water and aqueous solutions of different pH. Under low pH multilayer formation and crystallization effects in the layers were visualized by recording the hystereses in the Langmuir–Blodgett isotherms and by transferring the layers onto substrates: mica, modified mica to make it positively charged, and gold (111). AFM images exhibited platelets of multilayer phase. The initial stage of liquid adsorption layer was clearly seen in the isotherms when the subphase contained ions and neutral or alkaline pH. The nature of this initial adsorption layer and its organization was studied in-depth by the EC STM method using Au(111) as the substrate and applying different potentials to it. A model showing the arrangement of hydrogen bonds between adsorbed molecules is presented and related to the observed organization of the layer.

Electrochemically Addressable Metal Nanoparticles Deposited in Short Tantalum Oxide Nanotubes

Corie A. Horwood and Viola I. Birss
University of Calgary
2500 University Drive NW, Calgary, Canada
birss@ucalgary.ca

We have recently reported the formation of films of highly ordered Ta oxide (Ta_2O_5) nanotubes (NTs) by the electrochemical anodization of Ta foil in a two-electrode cell configuration. [1] These NTs are typically 1 to 15 µm in length, although shorter NTs can be formed by decreasing the HF concentration and anodization time employed. Ta oxide is biocompatible, chemically stable, and forms high surface area ordered oxide structures, qualities which make it an interesting material for a variety of applications. One of the long-term goals of this work is to employ Ta_2O_5 NTs, in combination with biocompatible and redox-active Ir oxide nanoparticles (NPs) and the enzyme Glucose Oxidase (GOx), in order to form an amperometric glucose biosensor.

Similar to what has been developed for Ti, Zr, etc.,[2] a simple, one-step method of electrochemical anodization of Ta in an aqueous solution containing HF, H_2SO_4 and H_2O has been used to form stable ordered Ta oxide NTs of varying diameter (by changing anodization voltage) and length (by changing anodization time and/or HF concentration), including as short as 50 nm. The Ta oxide NTs are characterized by very good adhesion to the Ta substrate and NT diameters of ca. 25 nm (for anodization at 15 V). After anodization, deposition of a range of metals (Pt, Au, Ag, Ir), followed by thermal annealing, was used to form metal NPs by a thermal dewetting process.

Prior to annealing, the Ta electrochemistry is completely blocked by the deposited metals. After annealing, the metal NPs formed in the pores of short (≤ 200 nm) Ta oxide NTs are electrochemically addressable, despite the presence of a thin (ca. 4 nm) barrier (compact) oxide layer at the base of the NTs. The metal NPs contained in the NTs can be made to undergo surface reactions typical of their bulk behaviour. These highly ordered NP arrays are of interest for catalysis and biosensing applications.

References

(1) El-Sayed, H. A.; Birss, V. I. *Nanoscale* **2010**, *2*, 793–8.
(2) Macák, J. M.; Tsuchiya, H.; Ghicov, A.; Yasuda, K.; Hahn, R.; Bauer, S.; Schmuki, P. *Curr. Opin. Solid State Mater. Sci.* **2007**, *11*, 3–18.

Characterizing fluorophore labeled DNA-SAMs using electrochemical induced orientation changes and impedance methods.

Jannu Casanova-Moreno and Dan Bizzotto
AMPEL, Dept. of Chemistry, University of British Columbia, Vancouver, BC, CANADA
bizzotto@chem.ubc.ca

The modification of gold surfaces with DNA self-assembled monolayers have been studied in detail[1]. Labeling the DNA with a fluorophore opens new signal transduction possibilities when used as a biosensor. One bio-sensing system that has been demonstrated by Rant [2] involves the use of such a DNA-SAM in an electrochemical cell. The change of potential, which results in a change in electrode surface charge, induces a change in the orientation of the DNA molecules, attracting them to the interface, thereby decreasing the measured fluorescence, or repelling them, increasing the fluorescence. The response of these layers was found to depend on the density of adsorption, the electrolyte concentration and the rate at which the potential is changed. In this work, we investigate the modified surface of a gold bead electrode with in-situ fluorescence microscopy coupled with electrochemistry[3]. The response of the fluorescence intensity from the interface is measured as a function of the potential perturbation frequency, and a fluorescence-impedance spectra are created for specific regions of the surface (~100um in diameter). The response of the DNA SAM to the potential of the interface, rather than the applied potential, is calculated. The rate at which DNA changes orientation is examined as a function of the electrochemical variables and the nature of the DNA SAM.

References

(1) Tornow M, Arinaga K, Rant U. Electrical Manipulation of DNA on Metal Surfaces. NanoBioTechnology. 2008;187–214.
(2) Kaiser W, Rant U. Conformations of end-tethered DNA molecules on gold surfaces: influences of applied electric potential, electrolyte screening, and temperature. J. Am. Chem. Soc. 2010;132(23):7935–45.
(3) Murphy JN, Cheng AKH, Yu HZ, Bizzotto D. On the nature of DNA self-assembled monolayers on Au: measuring surface heterogeneity with electrochemical in situ fluorescence microscopy. J. Am. Chem. Soc. 2009 Mar 25;131(11):4042–50.

Investigation of the solid electrolyte interphase between graphite electrode/ ionic liquid electrolyte

Ewelina Bolimowska[1,2], Catherine C. Santini[2], Helene Rouault[1]
[1]*CEA-Liten, 17, rue des Martyrs 38054 Grenoble Cedex 9, France*
[2]*Université de Lyon, Institut de Chimie de Lyon, UMR 5265 CNRS-C2P2, 43 Boulevard du 11 Novembre 1918, 69616 Villeurbanne, France*
ewelina.bolimowska@cea.fr

Lithium ion batteries are extensively used as the power source for the consumer electronics, such as mobile phones and laptops due to their high voltage and high energy density (smaller and smatter technologies) (1). They are the most promising option for the next generation of the hybrid and electric vehicles. Extensive study is focus to increase their safety due to the use of flammable organic carbonate electrolyte (2) and their capacity loss resulting from the reactions of the electrolyte onto the electrode surface (3). The electrolytes derived from ionic liquids (ILs) have gained a lot of attention due to their thermal and electrochemical stability, flame retardant performance and high ionic conductivity (4-5). Nevertheless, the poor cycling observed with IL-electrolytes in devices using graphite electrode (Cgr) as anode is a significant drawback for implementation of these systems in industrial production. The aim of this work is focused on the understanding of the formation ionic liquid based electrolyte/graphite interphase. For this purpose, device containing the graphite (Cgr) and lithium electrodes, glass fiber separator along with electrolyte based on the mixture of (1-hexyl-3-methylimidazolium (bis(trifluoromethanesulfonyl) imide) $C_1C_6ImNTf_2$ with $LiNTf_2$ ($1 mol.L^{-1}$) and 5%vol. VC (vinylene carbonate) referred as $[C_1C_6Im[Li][NTf_2][VC]]$ has been examined. Firstly, the wetting time of graphite by $[C_1C_6Im[Li][NTf_2][VC]]$ in three-electrode Swagelok cells at 25°C and 60°C has been determined by electrochemical impedance spectroscopy (EIS). Then, the evolution of Cgr electrode surface, of the described cell, before and after cycling (2 and 5 cycles, C/20 at 60°C) was studied by FIB-SEM technique. This analysis proved that a SEI layer thickness of ~ 90 nm has been formed. The characterization of this film is under progress and will be discussed in the communication.

References:
1. J.-M. Tarascon, M. Armand, *Nature*, 2001, **414**
2. S.-Y. Bae, E-G. Shim, D-W. Kim, *J. Power Sources*, 2013, 1-6
3. J. T. Lee, N. Nitta, J. Benson, et al., *CARBON*, 2013, **52**, 388-397
4. J.-K. Park, *Wiley-VCH, Weinheim*, 2012
5. H. Srour, H. Rouault, C. Santini, *J. Electrochem Soc,* 2013, **160**, 781-785

Electrochemistry in non-conventional electrolytes: case of the [BMIm][DCA] room temperature ionic liquid - gold interface

S. Vanderaspoilden, A. Meunier, R. Michez, J. Christophe, Th. Doneux and C. Buess-Herman,
Chimie Analytique et Chimie des Interfaces, Faculté des Sciences, Université Libre de Bruxelles
Boulevard du Triomphe, 2, CP 255, B-1050 Bruxelles, Belgium
cbuess@ulb.ac.be

Room temperature ionic liquids (RTILs) have unique physicochemical properties, such as low vapour pressure, reasonable thermal stability and large potential window. Recently, they have been increasingly used as media in many electrochemical processes such as electrodeposition or energy storage devices. Surprisingly little is known on the structure and properties of the interfacial region in these non-conventional electrolytes although this is a key to understand the electrochemical reactivity of electrode-RTIL interfaces in order ultimately to design interfaces for specific applications.

Besides following the traditional strategy consisting in the acquisition of data characteristic of the electrode in contact with a pure RTIL, we also use an alternative way to probe the interface in presence of RTIL. Information on the interfacial behaviour of the RTIL will be gained through the competitive adsorption that will occur at the electrode between the ionic liquid and other adsorbates. The project will therefore be developed along two main lines: competition for surface occupancy between the ionic liquid and water on the one hand, and between the ionic liquid and organic additives on the other hand.

In this work we focus on the 1- butyl -3- methylimidazolium dicyanamide or [BMIm][DCA]-gold interface. The RTIL is particularly interesting in the context of the electrochemical deposition of metals since the DCA anion can complex many metal salts. Copper species (Cu(0), Cu(I) and Cu(II)) are here taken as redox probes. The electrochemical behaviour of copper ions is studied at the gold-[BMIm][DCA] interface by combining various electrochemical techniques (voltammetry, chronoamperometry, chronopotentiometry) and electrochemical quartz-microbalance measurements.
Impedance measurements will complemented the data in order to discuss the influence of the addition of water and of an organic additive such as uracil on the characteristics of these redox systems at the [BMIm][DCA] – gold electrode.

Spectroelectrochemistry Using Synchrotron Infrared Radiation

Ian J. Burgess, Scott M. Rosendahl, M. Lardner, Kaiyang Tu
University of Saskatchewan, Department of Chemistry
110 Science Place, Saskatoon, SK, Canada
ian.burgess@usask.ca

Synchrotron infrared radiation has been successfully coupled through an IR microscope to a thin-cavity external reflectance cell to study electrochemical processes. Excellent signal-to-noise ratios were achieved even at aperture settings close to the diffraction limit. Comparisons of noise levels as a function of aperture size demonstrate that this can be attributed to the high brilliance of synchrotron radiation relative to a conventional thermal source. Time resolved spectroscopic studies of diffusion controlled redox behaviour have been measured and compared to purely electrochemical responses of the thin-cavity cell. Marked differences between the two measurements have been explained by analysing diffusion in both the axial (linear) and radial dimensions. Whereas both terms contribute to the measured current and charge, only species that originate in the volume element above the electrode and diffuse in the direction perpendicular to the electrode surface are interrogated by IR radiation. Implications for using ultramicroelectrodes and synchrotron IR (SIR) to study electrochemical processes in the sub millisecond time domain will also be presented including preliminary, electrochemical time of flight experiments.

Structure-Activity Relationships in Electrocatalysis at Individual Carbon Nanotubes using Scanning Electrochemical Cell Microscopy (SECCM)

J.C. Byers, A.G. Güell, P.R. Unwin
Department of Chemistry, University of Warwick
Coventry, CV4 7AL, United Kingdom
j.c.byers@wawick.ac.uk

The possibility of exploring the electrochemical response of nanomaterials at high spatial resolution, including individual nanoparticles and carbon nanotubes (CNTs), has recently been realized through the advent of Scanning Electrochemical Cell Microscopy (SECCM). [1-3] Furthermore, in combination with other complementary spectroscopic techniques, and using simple outer sphere redox probes, the local electrochemistry of pristine individual CNTs has recently been correlated with their electronic and structural properties for the first time. [2]

Due to their large surface areas and high electronic conductivity, CNTs have traditionally been considered as support materials for electrocatalytic applications. However, recent examples of the oxygen reduction reaction (ORR) at modified carbon nanotube electrodes, free of precious metal catalysts, highlights that the CNT itself may play a role. There is thus a need to understand the role of pristine carbon nanotubes for the ORR. In this work, we used a multi-probe approach, combining SECCM and other techniques to understand the influence of CNT local structure on the ORR at pristine individual CNTs. We make use of the high spatial resolution of SECCM to observe heterogeneous surface electroactivity arising from structural variations (straight vs. kinked CNTs) as well as to investigate surface modified (pristine vs. oxidized) sections of individual CNTs. The significance of these new results and insights will be discussed in view of the role of CNTs for electrocatalysis.

[1] N. Ebejer, A.G. Güell, S.C.S. Lai, K. McKelvey, M.E. Snowden, P.R. Unwin, Scanning Electrochemical Cell Microscopy: A Versatile Technique for Nanoscale Electrochemistry and Functional Imaging, Annu. Rev. Anal. Chem. 6 (2013) 329.
[2] A.G. Güell, K.E. Meadows, P.V. Dudin, N. Ebejer, J.V. Macpherson, P.R. Unwin, Mapping Nanoscale Electrochemistry of Individual Single-Walled Carbon Nanotubes, Nano Lett. Article ASAP, DOI: 10.1021/nl403752e
[3] S.C.S. Lai, P.V. Dudin, J.V. Macpherson, P.R. Unwin, J. Am. Chem. Soc., 133 (2011) 10744.

Size-dependent Reduction to Synthesize Hierarchical Porous Si Particles with Reversible Morphology Evolution

Qiangfeng Xiao, Yang Li, Mei Cai*
General Motors Research and Development Center,
30500 Mound Road, Warren, MI 48090, USA.
Phone: 586-596-4392; Fax: 586-986-1910; Email: mei.cai@gm.com

Silicon has attracted great interest as one of the most promising anode candidates for high energy lithium-ion batteries. The practical applications require that the electrodes have great capacity, high efficiency and long cycle life. Various Si nanostructures including nanoparticles, nanowires, nanotubes, and porous structures have been exploited to improve the stability through the accommodation of volume changes during cycling. Herein, we report a size-dependent reduction to synthesize hierarchical porous Si particles which demonstrate dominant inward expansion upon lithiation and reversible morphology evolution during charge/discharge process. Such behaviors make the electrodes in half cells operate over 500 cycles at 0.5C with a reversible capacity of ~1500 mAh/g. The synthesis method provides a new avenue for the rational design of nanomaterials with unique properties and is applicable to fabricate hierarchical structures of metals and semiconductors.

Surface-enhanced Infrared Spectroscopic Investigation of Reactions of Methanol and Ethanol at Pd Electrodes in Alkaline Media

Yao-Yue Yang, Wen-Bin Cai*
Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, Fudan University, Shanghai 200433, China
E-mail:wbcai@fudan.edu.cn

It is of fundamental interest and practical importance to probe dissociations and oxidations of methanol and ethanol at Pd electrodes in alkaline media for developing Pt-free direct alkaline alcohol fuel cells (DAAFCs)[1]. So far, there are very few molecular level relevant studies as compared to those on Pt electrodes in acidic media. Here, we report our recent work on applying surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) and external mode IRAS in conjunction with electrochemical measurement and isotope labelling to probe the related surface reaction processes at Pd electrode.[2,3]

Regarding the methanol dissociation,[2] spectral data have shown a step-wise dehydrogenation to form CO_{ad} at Pd electrode at open circuit potential as well as at potentials lower than ca. -0.10 V. With increasing potential, a complete methanol oxidation to CO_2 (or (bi)carbonate) at Pd electrode can be envisioned, involving CO_{ad} and interfacial formate as the intermediates. The formate is also aby-product due toan incomplete methanol oxidation.

As for ethanol dissociation and oxidation,[3] it is manifested that adsorbed acetyl is a pivotal intermediate that may either decompose to C1 species (CO_{ad} and CH_x), or be oxidized to acetate (or to CO_2); the conversion of adsorbed CH_x to CO_{ad} at high potentials is also viable. Inhibiting direct oxidation of adsorbed acetyl to acetate could be effective for enhancing the desired C1 pathway for EOR.

The present work demonstrates that the combination of ATR-SEIRAS and traditional IRAS is very useful to give more reliable mechanistic analysis. It also provides a hint for the development of Pd-based anode catalysts for DAAFCs.

Acknowledgement:
This work is supported by NSFC (Nos. 21073045 and 21273046), SMCST (Nos. 11JC1402000 and 08DZ2270500).

References:

[1] Bianchini, C.; Shen P. K. *Chem Rev* 2009, 9, 4183.
[2] Yang, Y. Y.; Ren, J.; Zhang, H. X.; Zhou, Z. Y.; Sun, S. G.; Cai, W. B., *Langmuir*, 2013, *29*, 1709.
[3] Yang, Y. Y.; Ren, J.; Li,Q. X.; Zhou, Z. Y.; Sun, S. G.; Cai, W. B., to be published.

Nanomaterials Based Electrochemical Biosensors for Medical Applications

Aicheng Chen, Bal Ram Adhikari, Maduraiveeran, Govindhan, Sanghamitra Chatterjee, Asieh Ahmadalinezhad and Badal Shah
Department of Chemistry, Lakehead University
955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada
achen@lakeheadu.ca

Electrochemical biosensors are highly attractive for the monitoring of glucose, cholesterol, cancer, infectious diseases, and biological warfare agents. The immobilization of protein/enzyme on solid substrates for biosensing is a promising approach given the rapid advances in biotechnology and nanotechnology. Nanostructured materials have been receiving great attention in the development of electrochemical biosensors.

Recently, my research team has designed and synthesized a number of novel nanomaterials. In this presentation, we will briefly report on the development of electrochemical biosensors based on nanomaterials for biomedical applications. For instance, the immobilization of enzymes on nanoporous Au was explored for the electrochemical detection of glucose and cholesterol. Our study has shown that nanoporous Au provides an excellent matrix for the immobilization of the enzymes owing to its large surface area and strong adsorption ability for enzyme binding, high chemical stability, low inherent toxicity and high conductivity. The fabricated biosensors show very low Michaelis-Menten constants (2.1 mM for glucose and 0.64 mM for cholesterol), high sensitivity (177 μA/mM for glucose and 29.33μA/mM for cholesterol), low detection limits, and anti-interferents property. The co-immobilization of horseradish peroxidase and methylene blue on functionalized carbon buckypaper exhibits high electrocatalytic activity in response to hydrogen peroxide. The biological relevance of the developed biosensor has also been studied by the determination of hydrogen peroxide in human urine samples of normal volunteers, prior to, and following the ingestion of coffee. Increased levels of urinary hydrogen peroxide concentration suggest that oxidative stress is induced by coffee drinking in humans. The significant roles of nanomaterials in electrochemical biosensing will be discussed

Advanced Catalysts for Oxygen Reduction Reaction in PEM Fuel Cells

Zhongwei Chen*, Drew Higgins, Aiping Yu, Rongyue Wang
Department of Chemical Engineering, Waterloo Institute for Nanotechnology,
Waterloo Institute for Sustainable Energy, University of Waterloo,200 University
Avenue West, Waterloo, Ontario, Canada N2L 3G1
E-mail: zhwchen@uwaterloo.ca

Proton Exchange Membrane Fuel cells (PEMFCs), fueled by hydrogen or methanol, have been considered promising for powering vehicles, residential applications, and portable electronic devices. Widespread commercialization of fuel cells hinges, however, on further reduction in materials cost, improvements of component durability, and increase in overall PEMFC efficiency. At the heart of the PEMFC are the anode catalyst layer, the cathode catalyst layer, and the proton exchange membrane. For the catalysts, the longstanding goals have been low cost, high catalytic activity for oxygen reduction reaction (ORR) and viable durability.

This talk will summarize the recent progress in the development and characterization of oxygen reduction electrocatalysts at Waterloo by focusing on the following two topics:

I. Pt Nanowire and nanotube electrocatalysts: One-dimentional Pt nanowires and nanotubes with remarkable durability and high catalytic activity has been developed by surfactant, surfactant-free or electrospinning methodologies. Due to their unique combination of dimensions at multiple length scales, the Pt nanowires and nanotubes can provide high Pt surface area by their nanometer-sized wall thickness and have the potential to eliminate or alleviate most of the degradation pathways of the commercial carbon supported Pt catalyst (Pt/C) and unsupported Pt black as a result of their micrometer-sized length.

II. Non-precious metal electrocatalysts: The Fe-SPc, with a novel structure inspired by that of naturally occurring oxygen activation catalysts is prepared by a non-pyrolyzing method, allowing adequate control of the atomic structure and surface properties of the material. Significantly improved ORR stability of the Fe-SPc is observed compared with the commercial Fe-Pc catalysts. The Fe-SPc has similar activity with the commercial Fe-Pc initially, while the Fe-SPc displays 4.6 times higher current density than that of the commercial Fe-Pc after 10 sweep potential cycles, and a current density 7.4 times higher after 100 cycles. This has been attributed to the incorporation of electron donating functional groups, along with a high degree of steric hindrance maintaining active site isolation. Non-precious metal Fe-SPc is promising as potential alternative ORR electrocatalyst for PEM fuel cells.

Titanium Oxynitride Supported on Graphene-Based Carbon Sheets as Oxygen Reduction Reaction Catalyst in Acid Media

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

The use of excessive amounts of rare and expensive platinum group metal (PGM)-based oxygen reduction reaction (ORR) catalysts has severely limited the widespread adoption of polymer electrolyte fuel cells (PEFCs). State-of-the-art non-PGM catalysts are usually supported on carbon-based materials such as amorphous carbon blacks, carbon nanotubes etc, or supported on materials prepared by the carbonization of a polymer-based precursor. Besides contributing to the electrical conductivity, different roles of carbon-based materials were demonstrated: a catalyst support or an active site, or both. However, for these roles, only the surface of the carbon material is utilized, and not the bulk. In this regard, two-dimensional carbon-based materials such as graphene sheets should be ideal catalyst supports as they have a very large specific surface area. In this work, abundant and highly stable non-PGM catalysts, titanium oxynitride (TiO_xN_y) particles were supported on grapheme-based carbon sheets via various routes including a hydrothermal method [1] as shown in Fig. 1. Two different lattice spacings of 3.2 Å and 2.2 Å, which were assigned to the (1 1 0) and (1 1 1) plane of rutile were observed. The rutile TiO_2 phase doped with nitrogen without using conventional ammonia gas treatment emerged to be more active toward ORR than the anatase for the first time.

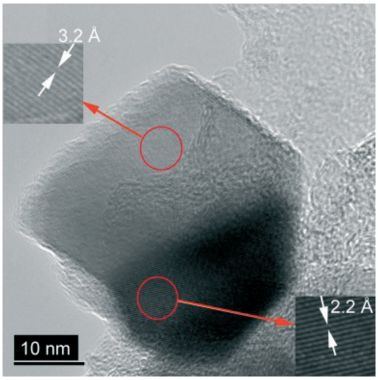


Fig. 1. A field emission-transmission electron microscopy image of hydrothermally-synthesized TiO_xN_y supported on reduced grapheme oxide sheets.

Acknowledgments
This work was partially supported by the Adaptable and Seamless Technology Transfer Program through Target-driven R&D, AS231Z03618C, from JST.

Reference [1] M. Chisaka and H. Muramoto, ChemElectroChem in press.

Preparation and Characterization of Conducting Polymer (PANI) Decorated by Functionalized Multiwalled Carbon Nanotubes

Ipek Becerik , Muge Civelekoglu,
Chemistry Department, Istanbul Technical University, Maslak-Istanbul/Turkey
becerik@itu.edu.tr

Intrinsically conducting polymers are known as synthetic metals and have been studied extensively due to their intriguing electronic -redox properties and applications in many fields.On the other hand, carbon nanotubes (CNTs) have attracted considerable interest owing to their application in fabricating a new classes of advanced materials because of their unique structural, mechanical and electronic properties. Therefore the formation of CNTs/functional polymer composites would be a meaningful way to improve or extend the properties of polymers or CNTs. Electrochemical polymerization provides a convenient approach to fabricate CNTs/conducting polymer nanocomposites. In particular, these composites with strong interactions between the MWCNTs and conducting polymers were demonstrated to facilitate electron/hole transport. Polyaniline (PANI) with a high application potential is an important polymer for the synthesis of such nanotube composites suitable for improved structural of functional applications. In current study, a new PANI/functionalized multi-wall carbon nanotube composite (fMWCNTs) has been succesfully synthesized by an in-situ electropolymerization process in acidic media. Reaction conditions were optimized in terms of aniline, fMWCNTs and acid concentrations, sweep rate,etc. Cyclic voltammetry was used thoroughout the study. SEM images showed both complete and partial coating of PANI on the surfaces of nanotubes. Moreover , from FTIR spectrum of PANI-MWCNTs, it was seen that the MWCNTs were covered by PANI films providing good stability X-ray diffactograms of PANI films were taken depending on different amount of MWCNTs compositions,as well. Prepared surfaces were tested on the electrooxidation of alcohols as electrode material in fuel cell applications.

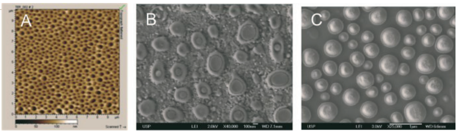
References

[1]X.Liu,W.Zhang,C.Wang,T.Wen,Y.Wei,ProgressinPolymer Science,36(2010)67
[2] A.N.Grace, K.Pandian, Electrochem.Commun., 8 (2006), 1340.
[3] V.Selvaraj, M.Alagar, Electrochem. Commun., 9 (2007) 1145.

Structuration of gold macropatterns over conducting and non-conducting substrates

Susana I. Córdoba de Torresi, Rafael N.P. Colombo, Vinicius R. Gonçales, Denise F.S. Petri
Instituto de Química, Universidade de São Paulo
Avenida Prof. Lineu Prestes, 748, Cidade Universitária, São Paulo, SP, Brazil.
storresi@iq.usp.br

The structuration of polymeric films has been a field of great interesting due to the possible applications in catalysis, anti-reflex surfaces and also like template membranes, as explored here with poly(methyl methacrylate) (PMMA). The formation of the structured PMMA membranes can be achieved by spin-coating, and the thickness of the resulting films depends on the concentration of the polymer, polymer molecular weight, spinning velocity and spinning time. Moreover, the structuration of the films are controlled by the solvent used for dissolving the polymer, the balance of energies related to the substrate/polymer and substrate/solution interactions, relative humidity and solution viscosity. [1] The formation of cavities occurs because during the spin-coating process the volatile organic solvent evaporates, cooling the region close to the surface and favouring water vapour condensation as droplets on the solution surface. As PMMA is insoluble in water, the polymer is segregated from the water droplets. So, at the end of spinning-process, the water droplets evaporate, leaving the occupied volume free. [2] This process generates templates with pores on the surface (Fig.A). In this study, the optimization of the physical-chemical parameters involved in the formation of the porous PMMA membranes was investigated. Moreover, after obtaining the desired porous structure, these cavities were employed as template for electrodeposition of gold on conductive substrates. (Fig.B) It was investigated (i) the optimization of the charge density conditions, in order to fully occupy the free volume of the cavities without loss of the structuration; (ii) the effect of the kinetics involved during gold electrodeposited formation, which changed the size and the morphology of the formed structures and (iii) the methodologies employed to remove PMMA after gold electrodeposition, such as dissolution in different solvents or calcination. Finally, the PMMA membrane was also applied to deposit gold through sputtering, which can be employed in non-conductive substrates. Here, the thickness of the gold deposition into the cavity can be controlled directly through the equipment, leading to a substrate modified with gold macropatterns (Fig. C).



[1] A.F. Dário, H.B. Macia, D.F.S. Petri, Thin Solid Films 524 (2012) 185.
[2] G. Widawski, M. Rawiso, B. François, Nature 369 (1994) 387.

Ionic Liquid Structure at Mica and Graphene Interfaces

Nico E. A. Cousens[1], Florian Hausen[1], Alexander M. Smith[1], Kevin R. J. Lovelock[2], and Susan Perkin[1]*
[1]*Department of Chemistry, Oxford University, South Parks Road, Oxford OX1 3QZ, UK.*
[2]*Department of Chemistry, Imperial College London, London SW7 2AZ, UK*
** corresponding author: susan.perkin@chem.ox.ac.uk*

The structure of ionic liquids at charged surfaces is governed by a combination of electrostatic and other molecular interactions, and by ion-packing constraints. I will describe our experiments using a Surface Force Balance to detect the interaction between atomically smooth and negatively charged mica sheets across thin films of ionic liquids; the film thickness ranges from hundreds of nanometers down to a single ion diameter(1, 2). From the resulting oscillatory force profiles we can determine the layering structure of the ionic liquids. I will also report the initial findings of a study into the effect of electric fields applied across the film. Finally, I will discuss the development of a new instrument: the Graphene Surface Force Balance, which enables the study of liquids at the surface of graphene, with simultaneous control of the surface potential.

1. Perkin S, et al. (2011) Self-assembly in the electrical double layer of ionic liquids. Chemical Communications 47(23):6572-6574.
2. Smith AM, et al. (2013) Monolayer to Bilayer Structural Transition in Confined Pyrrolidinium-Based Ionic Liquids. The Journal of Physical Chemistry Letters 4(3):378-382.

Novel Selenophene and Tellurophene Derivatives From Electrochemistry to Working Devices

Przemyslaw Data[a,b], Piotr Pander[a], Radoslaw Motyka[a].
[a] *Silesian University of Technology, Faculty of Chemistry, Department of Physical Chemistry and Technology of Polymers, 44-100 Gliwice, Strzody 9, Poland*
[b] *Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 41-819 Zabrze, Curie-Sklodowskiej 34, Poland*
przemyslaw.data@polsl.pl

The study of new organic materials with potential photoluminescent properties, such as conjugated molecules and polymers featuring photo- and electroluminescent properties, has attracted exceptional interest in terms of molecular optoelectronics applications, e.g. as potential elements of electroluminescent diodes, displays and photovoltaic cells. Carbazole and its derivatives have been known for many years mainly due to their high hole transporting capabilities and strong fluorescence, as components of OLED devices. There are two types of carbazole derivatives, N-substituted-2,7-carbazole and N-substituted-3,6-carbazole in which they are quite different electronic and optical properties. Triphenylamine derivatives such as tris[4-(thiophen-2-yl)phenyl]amine are very stable trifunctional monomers for electropolymerization of films having high conductivity. Selenophene and tellurophene derivatives have lower oxidation potential in compare to its sulfur or oxygen analogs.

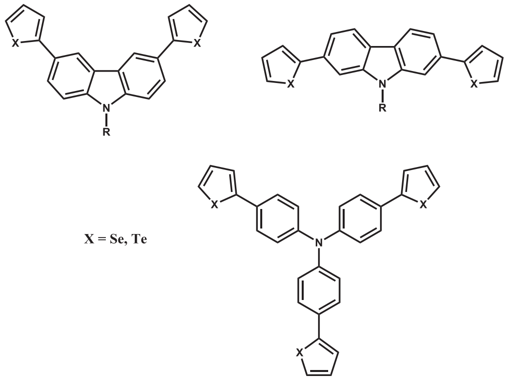


Fig.1 Investigated monomers.

In our work we will present a electrochemical, spectroscopic and electroluminescence characteristic of novel monomers (Fig.1) and their electrodeposited polymer

Acknowledgements. This work was supported by National Science Centre, Project No. 2011/03/N/ST5/04362 and Ministry of Science and Higher Education Project No. IP2012 039572.

Polyoxometalates as Electrode Materials for Molecular Cluster Batteries

Han-Yi Chen[1,2], Jochen Friedl[1,3], Rami Al-Oweini[4], Madhavi Srinivasan[1,2],
Ulrich Kortz[4], Ulrich Stimming[1,3,5]
[1] TUM CREATE, 1 CREATE Way, #10-02 CREATE Tower, Singapore
[2] School of Materials Science and Engineering, Nanyang Technological University, Singapore
[3] Department of Physics E19, Technische Universität München, James-Franck Str. 1, 85748 Garching, Germany
[4] School of Engineering and Science, Jacobs University, P.O. Box 750561, 28725 Bremen, Germany
[5] Institute for Advanced Study (IAS) of the Technische Universität München, Lichtenbergstr. 2a, 85748 Garching, Germany

Polyoxometalates (POMs) are a large class of transition metal oxide molecular clusters with well-defined structures. POMs are reported as promising active materials for energy storage applications due to their ability to undergo fast and reversible redox reactions.[1,2] The stability of the POMs is independent from the recoverability of its crystal structure, because they are expected to undergo redox process as a molecular cluster rather than a continuum.[2] In this study, vanadium-containing polyoxometalate (V-POM) are used as cathode materials for molecular cluster batteries. The electrochemical properties are investigated by cyclic voltammetry and charge-discharge galvanostatic analyzer. The V-POM molecular cluster battery provides high capacity up to 200 mAh g^{-1}, and exhibits excellent capacity retention up to 50 cycles which demonstrate that V-POM is promising electrode material for energy storage applications.

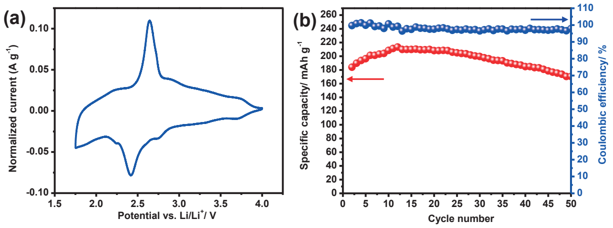


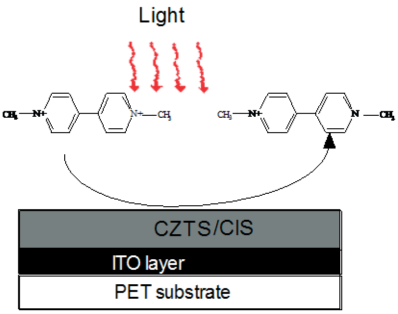
Figure 1. (a) The CV curve, and (d) the specific capacity and coulombic efficiency of V-POM molecular battery tested in 1 M $LiPF_6$ in EC/DEC.

[1] A. Cuentas-Gallegos, R. Martinez-Rosales, M. Baibarac, P. Gomez-Romero, and M. E. Rincon, Electrochem. Comm. 9 (2007) 2088.
[2] S. Uematsu, Z. Quan, Y. Suganuma, and N. Sonoyama, J. Power Souces 217 (2012) 13.

$CuInS_2$ and Cu_2ZnSnS_4 Nanocrystal Inks for Thin Film Solar Cells

Daniel Vaccarello[1], Amy Tapley[1], Matthew Turnbull[1], David A. Love[2,3], Po K. Lau[4] and Zhifeng Ding[1,2*]
[1]Department of Chemistry, [2]Surface Science Western, The University of Western Ontario, 1151 Richmond Street, London, ON N6A 5B7, Canada
[3]Rosstech Inc., 71 15th Line South, Orillia, ON L3V 6H1, Canada
CIS Scientific Inc, 3500 Matte Boul., Local 230, Brossard, QC J4Y 2Z2,Canada
zfding@uwo.ca

The efficiency, capital investment and production cost of photoelectroactive materials for $CuInGaSe_2$ (CIGS) type thin film solar cells have attracted much attention to researchers. Herein, $CuInS_2$ (CIS) and Cu_2ZnSnS_4 (CZTS) nanocrystals were easily prepared by one-pot reactions. The composition, structures and photoreactivity of the prepared nanocrystals were investigated by electron dispersive x-ray (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman microspectroscopy as well as scanning photoelectrochemical microscopy. Photoelectrochemistry was employed to investigate photoreactivity of the nanocrystal films, in a solution of methyl viologen to evaluate their photoconversion. Intensity Modulated Photocurrent Spectroscopy was utilized to assess photovoltaic processes at solution/thin film interfaces.



Acknowledgement

Financial supports from Ontario Center of Excellence and Natural Sciences and Engineering Research Council (SPG, I2I, CRD, DG, RTI) are very much appreciated.

Fabrication of potentiometric penicillin G biosensor based on co-entrapment of penicillinase and MWCNTs within polypyrrole film

Winston O. Doherty[a], Samuel B. Adelojua[a,*]
[a] *NanoScience and Sensor Technology Research Group, School of Applied Sciences and Engineering, Monash University, Churchill, Victoria 3842, Australia*
[a,*] *sam.adeloju@monash.edu ;* [a]*winston.doherty@monash.edu*

This study presents a strategy for the fabrication of highly sensitive, reproducible and cost effective electrochemical nanobiosensors for penicillin detection with the aid of multi-walled carbon nanotubes (MWCNTs). Penicillinase and MWCNTs were co-entrapped within polypyrrole (PPy) film via galvanostatic electropolymerisation and the biosensor was employed for potentiometric biosensing of penicillin G. Evidence of co-entrapment of penicillinase and MWCNTs into the polypyrrole matrix was established by electrochemical impedance spectroscopy (EIS). EIS was also used to observe the interfacial electron transfer at the PPy-P'Nase-MWCNTs electrode surface. The proposed biosensor utilized very small quantity of enzyme, lower than those of the reported potentiometric and amperometric penicillin biosensors, thereby minimizing cost of analysis and yet achieved a very high sensitivity of 113 mV/decade for potentiometric detection of penicillin G.

Overall, the fabricated biosensor offers interesting features including high sensitivity, low minimum detectable concentration of 5 μM, low response time of < 2 s and good recoveries in real sample analysis of spiked milk samples without pre-treatment. This study demonstrates that co-entrapment of penicillinase and MWCNTs within a conducting PPy matrix is an effective and efficient approach of fabricating a reliable and cost effective potentiometric biosensor for measurement of penicillin G.

References

[1] L.F. Kantiani, Marinella Barceló, Damiá Barceló, Damiá, TrAC Trends in Analytical Chemistry, 28 (2009) 729-744.
[2] J.R. Siqueira, Jr. Abouzar, M. H. Poghossian, A. Zucolotto, V. Oliveira, O. N., Jr. Schoning, M. J., Biosensor and Bioelectron, 25 (2009) 497-501.
[3] X.C. Zhang, L. Xu, Y. Wang, H. Zeng, Q. Zhao, Q. Ren, N. Ding, L., Journal of chromatography. B, Analytical technologies in the biomedical and life sciences, 878 (2010) 3421-3426.

*Corresponding author. E-mail address: sam.adeloju@monash.edu

Control and Optimisation of the Interfacial Architecture of Electrochemical DNA Biosensors

Th. Doneux [a], A. De Rache [a,c], E. Triffaux [a], A. Meunier [a], M. Steichen [b],
C. Buess-Herman [a]
[a] *Chimie Analytique et Chimie des Interfaces, Faculté des Sciences, Université Libre de Bruxelles, Boulevard du Triomphe 2, CP 255, B-1050 Bruxelles, Belgium*
[b] *University of Luxembourg, Laboratory for Energy Materials, 41, Rue du Brill, 4422 Belvaux, Luxembourg*
[c] *Univ. Bordeaux, INSERM, U869, ARNA Laboratory, European Institute of Chemistry and Biology, 2, Rue Robert Escarpit, 33600 Pessac, France*
tdoneux@ulb.ac.be

The analytical performances (selectivity, sensitivity, limit-of-detection) of biosensors are ultimately connected to the interfacial architecture of the sensing surface, which needs to be optimised. Self-assembly of a mixed monolayer of thiolated probes and diluent onto gold surfaces used in the design of biosensing platforms is nowadays commonly performed by a two step immobilisation procedure.

In this work the merits of a one step co-adsorption procedure is emphasized and it is shown that the ionic strength is a very efficient tool for a fine control of the surface concentration of the immobilised probe. Surface densities have been determined by ac voltammetry for redox-labelled probes and by *in situ* electro-fluorescence measurements for fluorescent-labelled probes. With the non-labelled DNA sequences chronocoulometric measurements were performed in the presence of dissolved hexaammineruthenium(III) cations.

The maximum probe density achievable at high ionic strength by the one step co-adsorption procedure is limited by steric constraints and depends on the structure of the sequence. Various thiolated DNA sequences (ssDNA and dsDNA, linear, hairpin, quadruplex) co-adsorbed with a common diluent, the 4-mercaptobutan-1-ol (MCB) have been used to discuss the structural factors affecting the maximum surface densities obtained for the different types of probe.

Application of the one step co-adsorption procedure to the optimisation of the analytical performances of a protein aptasensor is illustrated by building a sensor for the detection of thrombin, based on the thrombin binding aptamer (TBA) sequence.

Reference

Th. Doneux, A. De Rache, E. Triffaux, A. Meunier, M. Steichen, C. Buess-Herman, *ChemElectroChem* **2014**, doi: 10.1002/celc.201300145

Study of Cysteine Adsorption on Pt from Acid Media

André H. B. Dourado, Tércio F. Paulo, Daniel C. Rodrigues, Márcia L. A. Temperini, Paulo T. A. Sumodjo
Instituto de Química – Universidade de São Paulo
Av. Prof. Lineu Prestes, 748, 05508-000 São Paulo, SP; Brasil
dourado@iq.usp.br

Cysteine (CYS), because of its thiol group on its side chain is believed to be very important on proteins adsorption/immobilization phenomena [Zhou, Y., Yu, B., Levon, K. *Synthetic Metals* **142** (2004) 137] and possibly on surface modification/functionalization processes. This communication reports some results on the study of CYS electrochemical adsorption/oxidation on a platinized platinum electrode using cyclic voltammetry and SERS. CYS was adsorbed on the Pt surface either at open circuit or by the application of a constant potential, followed by a washing procedure of the electrode and running an anodic linear potential sweep in the supporting electrolyte to oxidize the previously adsorbed residue, SAS. An anodic current transient was recorded during the electrochemical step revealing that adsorption occurred via an oxidative process. The oxidation E/I profiles of the SAS, obtained by the two different adsorption procedures reveal that the same species is formed. The ratio SAS oxidation to adsorption charges, Q_{ox}/Q_{ads}, was found to be (5.2 ±0.1), which is explained by mechanism proposed by Pardac and Koryta [*J. Electroanal. Chem.* **17** (1968) 167]. From the analysis of the potentiodynamic E/I profiles obtained at different potential scan rates it can be easily inferred that the rate determining step of the SAS is a monoelectronic charge transfer. Thus, it can be considered that the above proposed mechanism is essentially correct with the exception that under the studied conditions step (II) is not an elementary step but complex and comprises a mechanism. From the cyclic voltammetry experiments with different CYS concentrations it was possible to determine an adsorption isotherm. A Temkin isotherm was the one that best fitted the data and the resulting heterogeneity factor, (46.75 ± 0.02) kJ mol^{-1}, reveals that a strong repulsive interaction exists between the adsorbed species. The SAS structure was studied spectroscopically using by borrowing SERS (bSERS), as Pt has low SERS activity [Zou, S., Weaver, M. J. *Anal.Chem.*70 (1998) 2387]. After the adsorption and washing of the electrode steps, the electrode was immersed in the cell containing the supporting electrolyte and the spectra were taken. Four bands are visible: at 595, 900, 990 and 1200 cm^{-1}. The first one is associated to the $\nu_{C\text{-}S}$, the 900 cm^{-1} band COOH bending, and the other two to the ν_{COOH}. Hence, cyc chemisorbs forming a Pt-S with strong physical interaction between the carboxyl group and the substrate.

CNPq. FAPESP.

The use of EIS measurements to determine the electrochemically active surface area of Pt

E. Bradley Easton, O' Rian Reid, Farhana S. Saleh
Faculty of Science (Chemistry), University of Ontario Institute of Technology
2000 Simcoe Street North, Oshawa, ON L1H 7K4 CANADA
Email: Brad.Easton@uoit.ca

The transmission line model has been used extensively over the last 2 decades to study PEM fuel cell catalyst layers [1]. When applied in the absence of a charge transfer process, detailed information about ion and electron transport can be determined. Furthermore, limiting (low frequency) capacitance has been shown to be a measure of active area [2]. However, since double layer capacitance originates from the surface area of both the Pt catalyst and the carbon support, quantitative measurement of the electrochemical surface area (ECSA) of Pt in fuel cell catalyst layers by electrochemical impedance spectroscopy (EIS) has not been possible.

To overcome this issue, our group has recently proposed a simple expression to relate faradaic pseudo-capacitance, C_F, determined by EIS with ECSA. By making two rapid and successive EIS measurements, 1 at a bias potential where H_{upd} occurs on Pt and another where only double layer capacitance is present, C_F for H_{upd} can be determined. A linear relationship between C_F and ECSA is expected for a surface bound process. To test this hypothesis, 2 different Pt/C catalysts were studied using an accelerated degradation testing protocol [3]. During the aging process, ECSA was monitored by CV and C_F was monitored by EIS. A linear relationship between C_F and ECSA was established, yielding proportionality constants that do not vary between catalysts. These constants can therefore be used to effectively determine ECSA values without performing CV measurements. An overview of our model and detailed description of its application will be presented.

References

1. M. C. Lefebvre, R. B. Martin, and P. G. Pickup, *Electrochem. Solid-State Lett.*, **2**, 259 (1999).
2. E. B. Easton and P. G. Pickup, *Electrochim. Acta*, **50**, 2469 (2005).
3. F. S. Saleh and E. B. Easton, *J. Electrochem. Soc.*, **159**, B546 (2012).

Theory of Platinum Mass Balance in Catalyst Layers of PEM Fuel Cells

Michael H. Eikerling, Steven G. Rinaldo
Department of Chemistry, Simon Fraser University,
8888 University Drive, Burnaby, BC, V5A 1S6, Canada
meikerl@sfu.ca

Since the invention of polymer electrolyte fuel cells in the 1960s, their platinum loading has been reduced by a staggering factor. This progress has been enabled, in large part, by the introduction of highly-dispersed nanoparticle catalysts as well as advances in porous electrode design.[1-3] Nevertheless, Pt remains a major concern of fuel cell developers in view of electrochemical performance, cost, durability and lifetime. The presentation will focus on degradation phenomena in nanoparticle-based catalyst systems that transform catalyst mass, catalyst surface area and electrocatalytic activity during fuel cell testing or operation.[4-6] We will present a recently developed dynamic theory of surface area loss phenomena based on the theories of Lifshitz and Slyozov, Wagner and Smoluchowski. The model couples continuity equations for Pt mass and particle size distribution with kinetic equations of surface processes. It rationalizes the temporal evolution of the particle size distribution and its moments. The developed theoretical-diagnostic methodology allows specific degradation fingerprints of Pt nanoparticle dissolution, Pt ion redeposition and particle coagulation to be identified. Application of the model to experimental degradation data establishes vital links between surface-area loss, Pt dissolution and Pt oxidation. To further scrutinize the underling relations between catalyst structure, oxidation state and dissolution kinetics, we develop an electrochemical kinetic model of oxide formation and reduction at Pt. It allows the current response measured in cyclic voltammetry to be de-convoluted and interpreted in relation to independent spectroscopic, imaging and theoretical data.

Acknowledgements
We gratefully acknowledge the financial support of this work by the Natural Sciences and Engineering Research Council of Canada as well as by the collaborating company, Automotive Fuel Cell Cooperation Corporation (AFCC).

References

[1] M. Eikerling, A.A. Kornyshev, and A.A. Kulikovsky, *Physical Modeling of Cell Components, Cells and Stacks*, in *Encyclopedia of Electrochemistry*, Vol. 5, ed. by D.D. Macdonald and P. Schmuki, ch. 8.2, p. 447 – 543, VCH-Wiley, Weinheim, 2007.
[2] *M. Eikerling, K. Malek, and Q. Wang,* Catalyst Layer Modeling: Structure, Properties, and Performance*, in* PEM Fuel Cell Electrocatalysts and Catalyst Layers*, ed. J.J. Zhang, 381-446, Springer, 2008.*

Towards the Understanding of Interfacial pH Scale at Pt(111) Electrodes.

Rubén Rizo, Elton Sitta, Enrique Herrero, Juan M. Feliu
Institute of Electrochemistry. University of Alicante.
Ap. 99. E-03080 Alicante. Spain
Juan.feliu@ua.es

Spectroelectrochemistry has shown that carbon dioxide is adsorbed at Pt(111) electrodes as carbonate or bicarbonate [1] in 0.1 M perchloric acid. In this respect, a systematic study of the adorbates from dicarboxilic acids shows bands that can be assigned to the dianion and to the hydrogenanion. Equal band population for both species would suggest that the second pKa is reached at the surface. This second pKa is more acidic at the surface than in solution, the difference being larger as the organic chain length decreases. In a similar way, detailed studies have shown that sulfate is the adsorbed species at Pt(111) electrodes, this adsorption also taking place at positive values of the potential of zero total charge of the interface [2]. It could be considered that the positive charge at the metal surface favors the deprotonation from the adsorbed molecules.

We can ask what happens to the water molecule, which has also labile protons. Eexperiments of CO charge displacement have been carried out at different pH solutions enable to calculate the potentials of zero total charge (pztc) and evaluate the potentials of zero free charge (pzfc). For these experiments, the total charge-potential curves in the SHE scale were calculated. These charge values were corrected according to the procedure proposed by M.J. Weaver [3]. From the corrected charge curves vs. potential, the pzfc for the different solutions were calculated by linear extrapolation. All the lines cross the zero charge point at the same potential. Moreover, two different slopes for the linear extrapolations are observed depending on the pH: at lower and higher pHs. One possible explanation is to consider that charge curves at lower pH would correspond to the interface populated with excess of protons, while the second linear dependence would correspond to the situation in which the dominant species is hydroxyl. At the crossing point, the interface would contain the same amount of protons and hydroxyl species, which should correspond to the neutral surface pH.

Aknowledgements
Financial support from MICINN project CTQ2010-16271 is acknowledged.

References.
[1] A.Berná, et al. J. Phys. Chem. B 108 (2004) 17928.
[2] Z. Su, et al. PCCP 12 (2012) 15231.

Bi and CO coadsorption on Pt nanoparticles

Marta C. Figueiredo, Marko Melander, Kari Laasonen, Tanja Kallio
Department of Chemistry, Aalto University
P.O. Box 16100, 00076 Aalto, Finland
1

The CO adsorption onto metallic surfaces has been subject of extensive study due to its importance in several reactions of interest like those involved in electrocatalytic energy production from small organic molecules (such as hydrogen, ethanol or formic acid) [1]. Moreover, CO is also considered a model molecule that can be used for understanding the reactivity of metallic surfaces [2].
Platinum based catalysts are considered the most active compounds for the majority of the electrocatalytic reactions concerning energy production. However, Pt can be easily poisoned by CO decreasing its activity. Recently, in our group it was shown that the adsorption of Bi in Pt nanoparticles increases the activity of this metal for both ethanol and methanol oxidation through a third body effect (avoiding poisoning of the surface by CO adsorption) [3,4]. In order to understand the effect of the adsorbed Bi on the CO adsorption on the Pt nanoparticles density functional theoretical (DFT) calculations for the adsorption energies of the co-adsorbed compounds were carried out using the CP2K/Quickstep software [5]. The calculations were performed in a Pt cluster of 147 atoms with a cuboctahedron geometry were Bi and CO were coadsorbed in different facets (111) and (100) and adsorption sites.
The results showed that Bi is very mobile on the Pt surfaces and the presence of CO increases that mobility leading Bi to adopt different positions on the surface [6]. Moreover, the coadsorption revealed to be very dependent on the surface site of Pt. For example, CO adsorption is stabilized by Bi in the (111) facet while the CO adsorption energy is lower for the (100) site. These results were compared with CO stripping experiments and a good agreement was obtained [6].

[1] M.T. M. Koper et al, Fuel Cell Catalysis: A Surface Science Approach (ed M. T. M. Koper), John Wiley & Sons, **2008**.
[2] K.J.J. Mayrhofer et al, ,Electrochem. Acta, 25-26, **2005**, 5144
[3] M. Figueiredo et al, App. Catalysis B: Environmental, 140–141, **2013**, 378
[4] M. C. Figueiredo et al, J. of Catalysis, submitted, **2013**
[5] J. VandeVondele, et al, Comp. Phys. Comm., 103 (**2005**), 167
[6] M.C. Figueiredo, in preparation

Comparative Studies of Conductive Nanostructures and Activation Properties in Solid Polymer Electrolytes

K.A. Friedrich[a,b], R. Hiesgen[c], S. Helmly[a,b], T. Morawietz[c]
[a] *German Aerospace Center, Institute of Technical Thermodynamics,*
Pfaffenwaldring 38-40, Stuttgart 70569, Germany
[b] *Institute for Thermodynamics and Thermal Engineering, University of Stuttgart,*
Stuttgart 70550, Germany
[c] *University of Applied Sciences Esslingen, Kanalstrasse 33, Esslingen 73728,*
Germany
andreas.friedrich@dlr.de

Solid polymer electrolytes are a key component in fuel cell as ion conducting barrier between the two electrochemical reactive electrodes and their conductivity significantly determines the performance of the cells. The conductivity of the electrolyte membranes is typically based on a nanoscale phase separation that results in an ionic conductive network and a stabilizing matrix. In sulfonated ionomers the sulfonic acid groups are solvated and a hydrophilic proton conducting aqueous ionic phase is formed in a self-assembling process upon solidification of the membrane. The hydrophobic polymer back-bones which may be perfluorinated as in case of Nafion-type molecules or aromatic as in case of multi-block copolymers provide mechanical stabilization. Consequently, the membrane properties at or close to the surface may differ from the bulk of the membrane and its structure and conductivity are crucial as interface between membrane and electrode/catalyst.

Different types of sulfonated membranes, perfluorinated Nafion® (**l**ong-**s**ide **c**hain molecules) and Aquivion® (**s**hort **s**ide **c**hain molecules) membranes, and aromatic multiblock copolymer membrane named JST (JSR Corp., Japan) have been investigated. Beside the investigation of surfaces freshly cut cross section from Nafion and Aquivion samples have been examined. For analysis material-sensitive and conducting atomic force microscopy was used to map local adhesion forces, stiffness, deformation, conductivity and surface potential with nanoscale resolution. The following issues will be addressed:

1. Change of the conductivity upon current flow.
2. Size and distribution of conductive area at the surface for various membranes.
3. Existence and thickness of a surface layer for different membranes.
4. Difference in membranes structure close to the surface.
5. Ionic structure of the bulk for Nafion® and Aquivion®**.**

Local Reactivity Indexes for Describing Changes in Properties during Electron Transfer Processes

Carlos Frontana, Rutely C. Burgos-Castillo, Eduardo Martínez-González
Centro de Investigación y Desarrollo Tecnológico en Electroquímica, SC
Parque Tecnológico Querétaro S/N, Sanfandila, Pedro Escobedo, Querétaro,
76703, Querétaro, México
cfrontana@cideteq.mx

Substituent effects are invariably related with electrodonating or electronwithdrawing capacities, as presented in the Hammett and Taft model. From a general chemical perspective, there are certain limitations of this model, concerning both its specific empirical definition and also the limited data of σ_x values. Therefore a valuable and general strategy for addressing substituent effect comes from the use of quantum chemical descriptors, which are properties calculated from electronic structure calculations on either a global or local scale for the reactive species. In order to test the validity of the proposed theoretical scheme based on variations of electronic distribution by the substituent effect, association processes of a series of electrogenerated anion radicals with the hydrogen bond donor 1,3-diethylurea, as well as studying reactive series in TEMPO structures are presented. Results of this analysis are presented and discussed in this work.

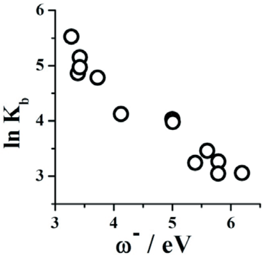


Figure 1. Relationship between experimental binding constants (K_b) and electrodonating power (ω^-) of substituted nitrobenzenes

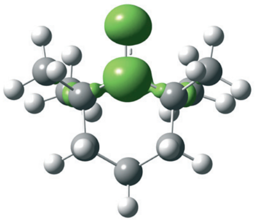


Figure 2. $f_{\alpha\alpha}(\mathbf{r})$ for TEMPO

Electrochemical and Chemical Formation of a Proton Transfer Complex Between the Quinone Dianion and Hydroquinone

Felipe J. González[a], Drochss P. Valencia[a], Miguel A. González-Fuentes[a], Carlos Frontana[b] and Pablo D. Astudillo[c]
[a]Departamento de Química del Centro de Investigación y de Estudios Avanzados del IPN. Av, I.P.N. 2508, 07360, D.F., Mexico
[b]Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Parque Tecnológico Querétaro, Sanfandila, 76703, Querétaro, Mexico
[c]División de Ciencias e Ingenierías del Centro Universitario de Tonalá, Universidad de Guadalajara. Morelos 180, 45400, Jalisco, Mexico.
fgonzale@cinvestav.mx

The electrochemistry of the 1,4-benzoquinone Q and hydroquinone QH_2 in acetonitrile and dimethylsulfoxide is analized to explain the nature of a broad reversible signal that appears during the reduction of quinones with small amounts of proton donors. This voltammetric wave cannot be explained in the framework of the classical square scheme mechanisms of the quinone reduction. Cyclic voltammetry and NMR experiments as well as electronic structure calculations were performed to show that under specific conditions, the anion QH^- disproportionates into a face-to-face dianionic quinhydrone associated by strong intermolecular hydrogen bonds. This complex explains the mentioned broad signal and the results presented show that it can be formed during the reduction of benzoquinone in the presence of stoichiometric amounts of weak proton donors such as acetic acid and hydroquinone, or by half-deprotonation of hydroquinone. An analysis of the energetic barriers of the hydroxyl protons involved in the complex is also presented.

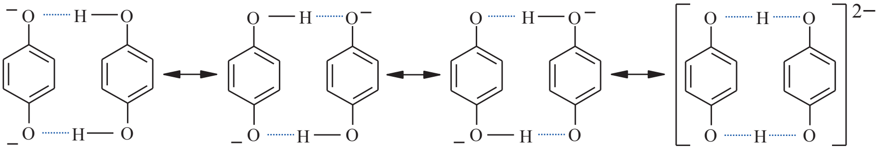


Figure 1. Proposed structures for the quinhydrone-type dianionic complex

On the use of porous and preferentially oriented {100} Pt electrode in electrocatalysis

Daniel Guay
INRS-Énergie Matériaux Télécommunications
1650 Blvd Lionel Boulet, CP 1020, Varennes, QC Canada J3X 1S2
guay@emt.inrs.ca

It is know from studies on single crystals that the rates of several electrochemical reactions are structure-sensitive. For example, in alkaline medium, the electro-oxidation of ammonia on Pt occurs almost exclusively on surface sites with (100) symmetry. Likewise, in acidic media, hydrazine adsorbs more readily on Pt (100) steps than on Pt (111) terraces, while the (100) planes are the most active planes. Therefore, careful tuning of the crystallographic surface orientation of an electrode can lead to drastic improvements in the activity, selectivity and stability of the catalyst.

In the present study, highly {100} oriented Pt deposits were prepared by electrodeposition from a 10mM HCl, 100 mM KCl and $Na_2PtCl_6.xH_2O$ electrolyte. The more oriented samples are made of pine tree-like structures that are effectively single crystals, with growth facets that are close to the {001} plane. The films are highly porous and roughness factors as large as 400 are obtained. The predominance of {100} facets is attributed to their energetically favoured growth in the presence of hydrogen, and is shown to be significantly enhanced when the mass transport of Pt^{4+} is limited. Due to the predominance of {100} facets, the normalized electrocatalytic activity ($\mu A.cm^{-2}{}_{Pt}$) for the electro-oxidation of hydrazine and ammonia is higher than non-oriented polycrystalline Pt by a factor of 4 and 2.7, respectively.

Formic Acid Oxidation Mechanism on Platinum Electrodes.

Juan V. Perales[1], A. Ferre-Vilaplana[2], Juan M. Feliu[1], Enrique Herrero[1]
[1]Instituto de Electroquímica, Universidad de Alicante,
Apdo. 99, E-03080 Alicante, Spain.
[2]Instituto Tecnológico de Informática, E-46022 Valencia, Spain, and
Departamento de Sistemas Informáticos y Computación, EPS de Alcoy,
Universidad Politécnica de Valencia, E-03801 Alcoy, Spain
**e-mail address: herrero@ua.es*

The role played by the different species (formic acid, solvated formate and adsorbed formate) and mechanisms involved in the formic acid oxidation on platinum electrodes is still subject of debate. To shed light into this issue, formic acid oxidation on platinum single crystal electrodes has been experimentally studied to determine the effects of pH, specific anions adsorption and Bi adatoms on the oxidation mechanism. It has been found that all of them, pH, adsorbed anions, and Bi adatoms, have an important effect on the oxidation currents. As has been already observed for polycrystalline electrodes [1], currents are proportional to the solution pH. Additionally, the specific adsorption of sulfate on the Pt(111) electrode has a positive catalytic effect on the oxidation. The activation energies estimated for the process indicate that adsorbed sulfate and pH diminishes the activation energy. Also Bi modified surfaces diminishes the activation energy. Considering the whole of these observations, and with the aid of DTF calculations, for the modified surfaces, an oxidation mechanism is proposed for the direct route. In this mechanism, solution formate should adsorb in a configuration in which the C-H bond is close the Pt surface. This adsorption mode is favored in the presence of adsorbed anions, formate or the Bi adatom.

Aknowledgements
Financial support from MICINN project CTQ2010-16271 is acknowledged.

References

1. J. Joo, T. Uchida, A. Cuesta, M.T.M. Koper, M. Osawa, J. Am. Chem. Soc. 135 (2013) 9991.

Faradaic Phase Transition of Adsorbed Viologens on HOPG Electrode Surface

Tomohiro Higashi, Takamasa Sagara
Graduate School of Engineering, Nagasaki University,
1-14, Bunkyo-machi, Nagasaki 852-8521, Japan
sagara@nagasaki-u.ac.jp

Introduction. Viologen adsorption layers on an HOPG electrode in many cases undergo a faradaic phase transition between a gas-like adsorption layer of oxidized form (V^{2+}) and a two-dimensional (2D) condensed monolayer of reduced form ($V^{\bullet+}$) [1]. The phase transition of dialkyl viologens appears as a pair of anodic and cathodic spike-like dc voltammetric peaks [2]. The transitions are known to be governed by the type and strength of attractive intermolecular interactions in the condensed phase. Therefore, substitution of aromatic groups for alkyl chains is intriguing to examine the effect of π-π interactions between viologens and with the HOPG surface upon the transition. This paper is devoted to comprehensive discussions on π-π interaction and anion effect upon the phase transition using the results for dibenzyl viologen (dBV) [3,4] and diphenyl viologen (dPhV) [5].

Experimental. A basal plane HOPG electrode surface was brought into contact with viologen solutions for voltammetric, electroreflectance (ER), and *in situ* STM measurements in an Ar gas atmosphere at room temperature.

Results and Discussion. In KCl solution, dBV exhibited a single-step faradaic phase transition to form a 2D condensed monolayer of $dBV^{\bullet+}$ as revealed by ER and STM measurements [3]. The face-to-face π-π stacking interactions with nearest neighbor molecules, both between $V^{\bullet+}$ moieties and between benzene rings, causes the formation of a 2D condensed monolayer. In high concentration KBr solutions, the phase transition emerged as a two-step process [4]. The first-step (at less negative potential) was ascribed to a formation of a mesophase of $dBV^{\bullet+}\ Br^{-}$. The absence of face-to-face π-π stacking of $dBV^{\bullet+}$ moieties in the mesophase was confirmed by ER measurement. The second-step was ascribed to a phase transition between the $dBV^{\bullet+}\ Br^{-}$ mesophase and a 2D condensed phase of $dBV^{\bullet+}$.

In KCl solution, $dPhV^{2+}$ takes a strongly adsorbed state on an HOPG surface, unlike dBV^{2+} [5]. The phase change of dPhV was not of the first-order. Strong π-π interaction of $dPhV^{2+}$ with HOPG surface hampers its sharp phase transition.

References. [1] T. Sagara, S. Tanaka, Y. Fukuoka, N. Nakashima, *Langmuir*, **2001**, *17*, 1620. [2] Y. Tanaka, T. Sagara, *J. Electroanal. Chem.*, **2008**, *619-620*, 65. [3] T. Higashi, Y. Shigemitsu, T. Sagara, *Langmuir*, **2011**, *27*, 13910. [4] T. Higashi, T. Sagara, *Electrochim. Acta*, **2013**, *114*, 105. [5] T. Higashi, T. Sagara, *Langmuir*, **2013**, *29*, 11516.

Lateral and vertical spatial control of electroactive film deposition for latent fingerprint enhancement

A. Robert Hillman,[1] Rachel M. Sapstead[1], Natalie Corden[1], Karl S. Ryder[1], Maximilian Skoda[2], Robert M. Dalgliesh[2], Erik Watkins[3], Robert Barker[3], Andrew Glidle[4]
[1]University of Leicester, Leicester LE1 7RH; [2]Rutherford Appleton Laboratory, Didcot, Oxfordshire, OX11 0QX, UK; [3]Institut Laue Langevin, Grenoble, Cedex 9, France; [4]Glasgow University, Glasgow, G12 8LT, UK
e-mail: arh7@le.ac.uk

Fingerprints provide unambiguous identification of an individual, a facility that is exploited in criminal and civil applications. In criminal investigations, this usually involves *latent* (non-visible) *fingerprints*, which require chemical or physical treatment to create a visible image. Most chemical treatments involve interaction of a reagent (powder, dye or cyanoacrylate) with the *fingerprint residue*. The efficacy of such treatments is limited by deterioration or loss of residue due to environmental exposure. In a complementary strategy, we have used the fingerprint residue as a template to direct electrochemically generated reagent to the *bare surface* between the deposited ridges, thereby creating a negative image of the fingerprint. On metallic substrates, the process may be driven electrochemically.

This templating concept was recently demonstrated using electrodeposited polyaniline [1] and PEDOT [2] films and their electrochromic properties were used to adjust the visual contrast of the fingerprint image. Here we consider two extensions of this approach with the common goal of improving the sensitivity, spatial resolution and optical adjustment of the technique. In the first case, we continue to use polymer optical *absorption*, but vary these characteristics through the use of copolymers. In particular, we explore the optical properties (simplistically, colours) of poly(pyrrole-co-3,4-ethylenedioxythiophene) as functions of co-monomer feedstock ratio, deposition potential and (after transfer to monomer-free electrolyte) applied viewing potential. In the second case, we pursue the use of polymer optical *emission*, by means of post-deposition functionalization of polymer (here, polypyrrole) with a fluorophore. This strategy raises interesting issues with regard to spatial distribution of film components, since image veracity is governed by *lateral* control of deposition of the polymer matrix and sensitivity by *vertical* control of fluorophore diffusion and binding in the polymer matrix.

[1] A.R. Hillman, and A. Beresford, *Anal. Chem.*, *2010*, **82**, 483.

[2] R.M. Brown and A.R. Hillman, *Phys. Chem. Chem. Phys.*, *2012*, **14**, 8653.

Interfacial Phenomena of Battery Electrodes Investigated by Surface Enhanced Raman Spectroscopy

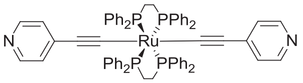
Bing-Joe Hwang[1, 2, *], Sunny Hy[1], Felix Felix[1], Yi-Hsiu Chen[1], Han-Ping Tseng[1],
Wei-Nien Su[1], John Rick[1], Delele Worku Ayele[1],
[1]Nanoelectrochemistry laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan
[2]National Synchrotron Radiation Research Center, Hsin-Chu, Taiwan
e-mail address: bjh@mail.ntust.edu.tw

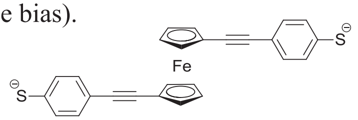
The use of surfaced-enhanced Raman spectroscopy (SERS) in lithium-ion battery and Li-O_2 battery studies has proven to be a powerful tool for observing the solid electrolyte interphase (SEI) growth, on the electrode's surface, that is crucial in determining the battery's electrochemical performance. However, until now, studies using SERS to observe SEI growth have been restricted to roughened Au or Ag electrodes and have given little consideration to electrode material effects. Here we have used shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) to investigate SEI layers on various battery electrodes and observe the SEI formation directly on the surface of the electrodes during charge and discharge. Several systems including electrodes (Si, layered compounds, S/C and Li) in lithium ion batteries and Li-S batteries will be reported in this presentation.

Single-molecule conductance of redox-active complexes using a novel automated I(s) STM methodology

Dr M. S. Inkpen, M. Lemmer, N. Fitzpatrick, Prof N. J. Long*, Dr T. Albrecht*
Imperial College London
South Kensington Campus, London SW7 2AZ
n.long@imperial.ac.uk; *t.albrecht@imperial.ac.uk*

A robust method to perform conductance measurements on a single-molecule scale was first described by Tao *et al.* in 2003 [1]. Their *in situ* scanning tunneling microscopy (STM) break-junction (*in situ* BJ) technique involves the repeated formation, measurement and breaking of hundreds or thousands of molecular junctions, whereby statistical analyses can be used to obtain reproducible junction characteristics. Other techniques have since been developed which complement and rival this approach, including the I(s) (current-distance) and I(t) (current-time) methods [2]. Whilst the *in situ* BJ regenerates a new STM tip for each junction measurement (introducing variation) and is normally restricted to measurements in condensed phases, the I(s) technique can utilize the same STM tip for all measurements and work in condensed/gases phases or even vacuum. Typically however the latter approach exhibits a lower molecular junction hit rate (number of I(s) spectra with molecular features vs. those without), so requiring some element of data selection (and introduction of possible bias).





Here, we will describe a novel *automated* I(s) approach, using macro-control for data collection and a mathematically rigorous data sorting algorithm (multi-dimensional vector-based component analysis). This methodology significantly decreases the STM time required to measure a molecule, and even permits unattended sessions. Furthermore, as the *grouping* of self-similar current-distance traces does not hide or misrepresent any of the total data set (all groups can be processed into histograms), this eliminates any associated bias. We stress that the separation of noisy/featureless spectra is almost always required when using the I(s) method, to permit the analysis of molecular characteristics with reasonable signal-to-noise. This new process has been applied to a range of model systems as well as previously uncharacterized redox-active molecules (figure) [3]. Results are rationalized in terms of charge transport mechanism and molecular structure [4].

[1] B. Xu *et al.*, *Science*, 2003, **301**, 1221. [2] R. J. Nichols *et al.*, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2801. [3] M. S. Inkpen *et al.*, *Organometallics*, 2013, **32**, 6053; M. S. Inkpen *et al.*, *Chem. Commun.*, 2014 (in preparation). [4] T. Albrecht, *Nat. Commun.*, 2013, **3**, 829; T. Albrecht *et al.*, *J. Am. Chem. Soc.*, 2006, **128**, 17132.

Oral presentation

Gaseous Nanobubbles at Solid/Liquid Interface: Implications for Surface Nanomorphology and Interfacial Processes

Pavel Janda, Hana Tarabkova
J. Heyrovsky Institute of Physical Chemistry ASCR
Dolejskova 3, 182 23 Prague 8, Czech Republic
pavel.janda@jh-inst.cas.cz

Surface nanobubles and micropancakes represent relatively stable gaseous nanostructures appearing at solid/liquid interface (Fig. 1a). While the plausible physical model of gaseous nanodomains is still searched, their existence is fully acknowledged, pointing to Knudsen gas behavior and charged gas/liquid interface respectively. As the surface occupation by nanobubbles can reach up to 90 %, depending on liquid saturation by gas, surface wetting properties, nanomorphology and other parameters, nanobubbles can be considered as a phenomenon affecting various interfacial processes. So far, the surface blocking manifested as irregularities in adsorption and (electro)deposition was resolved, while in gas evolution nanobubbles are expected to play the role of nucleus.

Nanobubble interaction with solid surface, ascribed to forces at nanobubble perimeter, pinning its ternary interface, appear to act in rearrangement of surface nanomorphology [1, 2] implying that nanobubble interfacial forces may exceed 10^2 MPa. Interestingly, nanobubble-assisted surface rearrangement manifested as imprints, can be utilized for ex-situ mapping of nanobubble appearance and revealed existence of surface nanobubble 2D aggregates (nano-foams) respectively (Fig. 1b).

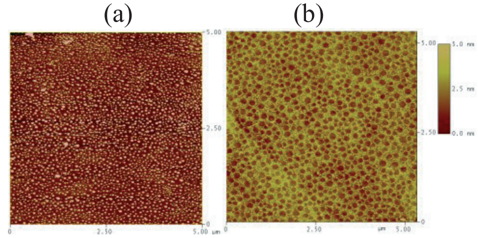


Figure 1: Solid surface immersed in water, densely covered by nanobubbles (a) and 2D nano-foam imprint (imaged by AFM *in situ* (a) and *ex situ* (b).

[1] P. Janda, H. Tarabkova *et al*: *Nanotechnology* 21 (2010) 095707
[2] H. Tarabkova, P. Janda: *J. Phys.: Condens. Matter* 25 (2013) 184001 (7pp)

Acknowledgement: GACR P208/12/2429

Cathodic Corrosion for Powder Materials

Yingchang Yang, Xiaobo Ji*,
Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China.
E-mail: xji@csu.edu.cn; Tel: +86-731-88879616;
Fax: +86-731-88879616

In contrast to metal cations, negatively charged homo-atomic polyanions, such as post-transition metals $[Pb_9]^{4-}$ anions and semimetal $[Ge_9]^{4-}$ anions, are seldom known to us owing to their versatile chemical reactivity with water and oxygen in air [1]. Here, electrochemically cathodic polarization of group 14 elements in N,N-dimethylformamide (DMF) solutions of quaternary ammonium salt have been developed to prepare nanostructured materials, which involves in-situ cathodic generation and subsequently Hofmann elimination (or oxidation by water) of the intermediate Zintl compounds $[R_4N^+]_4[E_9]^{4-}$ at room temperature [2]. Fig. 1 shows the typical transmission electron microscopy (TEM), high-resolution TEM and the corresponding SAED pattern of Pb powder materials. As can be seen, the as-prepared materail exhibits flower structures comprised of nanoflakes.

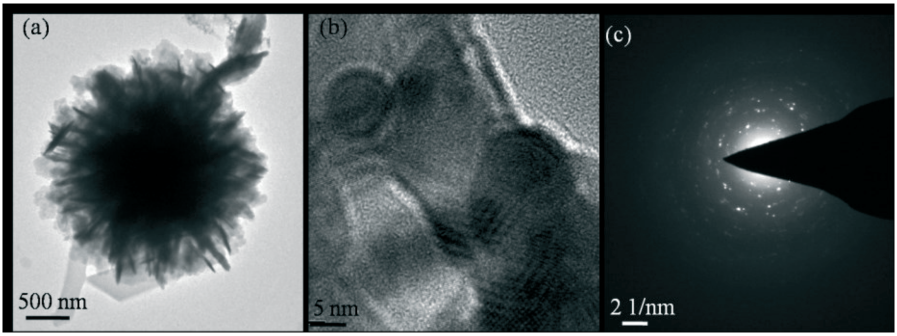


Fig. 1 (a) Typical transmission electron microscopy (TEM), (b) high-resolution TEM and (c) the corresponding SAED pattern of Pb powder materials prepared in DMF solutions.

[1] S.C. Sevov, J.M. Goicoechea, Organometallics, 25 (2006) 5678-5692.
[2] J.D. Corbett, Chem. Rev., 85 (1985) 383-397.

In Situ Electrochemical FTIRS Study of Ethanol Electrooxidation on Cubic PtRh Alloys Supported on Graphene

Lu Rao, Yan-Xia Jiang*, Bin-Wei Zhang, Yuan-Rong Cai, Shi-Gang Sun*
State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University,Xiamen 361005, (P. R. China)
Email: yxjiang@xmu.edu.cn

Cubic PtRh alloys supported on graphene (PtxRhy/GN) with different atomic ratio of Pt and Rh were directly synthesized for the first time using the modified polyol method with Br^- for the shape-directing agents. The X ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to characterize structure and morphology of these electrocatalysts. The results showed that they were composed of homogeneous cubic PtRh alloys. Traditional electrochemical methods, such as cyclic voltammetry and chronoamperometry, were used to investigate electrocatalytic properties of PtxRhy/GN towards ethanol electrooxidation. It can be seen that Pt_xRh_y/GN (x and y represent the atomic number of Pt and Rh) in all atomic ratio exhibited high catalytic activity. Electrochemical in situ FTIR spectroscopy was used to evaluate the cleavage of C–C bond in ethanol at room temperature in acidic solutions, the results illustrated that Rh in alloy can promote the split of C–C bond in ethanol, and the alloy catalyst with the atomic ratio of Pt:Rh = 1:1 showed an obviously better performance for the C-C bond breaking in ethanol and higher selectivity for the ethanol complete oxidation to CO_2 than alloys with other ratio of Pt and Rh. The investigation indicates that the enhanced activity of Pt_xRh_y/GN electrocatalysts is due to the specific shape of alloys and the synergistic effect of two metal elements as well as graphene support.

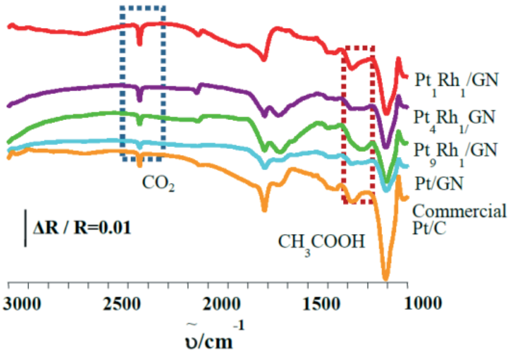


Figure 1 In situ SPAFTIR spectra of ethanol oxidation, E_R=-0.25 V, E_S=0.6 V, in 0.1 M ethanol and 0.1 M $HClO_4$ solutions. Band intensity comparisons of CO_2 with 1280 cm^{-1} of commercial Pt black and PtRh/GN at 0.6 V.

Interesting adsorption patterns of adsorbed organic compounds at Bi(111) electrode studied by in-situ STM and impedance spectroscopy methods

Heili Kasuk, Vitali Grozovski, Tavo Romann, Silvar Kallip, Enn Lust
Institute of Chemistry, University of Tartu
Ravila 14a, Tartu, 50411 Estonia
Heili.kasuk@ut.ee

Impedance spectroscopy and *in situ* STM methods have been used for investigations of the thiourea (TU), 4,4'- bipyridine (4,4'-BP) and 2,2'-bipyridine (2,2'-BP) adsorption at the electrochemically polished Bi(111) electrode from weakly acidified Na_2SO_4 supporting electrolyte solution [1,2,3]. In the region of maximal adsorption, the capacitance pits in the differential capacitance versus electrode potential curve have been observed. Based on the impedance data the heterogeneous adsorption and diffusion steps are the rate determining stages for TU, 4,4'-BP and 2,2'-BP adsorption at the Bi(111) electrode [1,2,3].

It was found that on Bi(111) at electrode potential E=-0.85V (vs Ag|AgCl in set HCl) TU adsorbs only at defect sites of Bi(111) single crystal [1], while 2,2'-BP gives very regular adsorption layer at Bi(111) in the region of zero charge potential (-0.6 to -0.4V vs Ag|AgCl) [2]. Differently from TU and 2,2-BP, 4,4-BP is forming a stripe pattern consisting of two type alternative rows. 4,4'-BP adsorption patterns also depend on the base electrolyte concentration. Adsorption from in less concentrated (0.05M) sodium sulphate 4,4'BP forms sparse compact adsorption layer if compared to 0.5M Na_2SO_4 base electrolyte solution . This is mainly caused by the comparatively strong van der Waals interaction of protonated 4,4'-BP molecules where the charge excess provided by 4,4'-BPH_2^+ is screened by sulphate ions coadsorption [3].

The cyclic voltammograms of 4,4'-BP at Bi(111) demonstrate that electrochemical processes at higher 4,4'-BP concentrations are quit irreversible, which are probably caused by the reduction of 4,4'-BP in two steps (electron transfer mechanism) and future formation of compact adsorption film on the electrode surface [3].

1. V. Grozovski, H. Kasuk, S. Kallip. E. Lust, Journal of Electroanalytical Chemistry 712 (2014) 103.
2. S. Kallip, H. Kasuk, V. Grozovski, P. Möller, E. Lust, Electrocemica Acta 53 (2008) 4035.
3. V. Grozovski, H. Kasuk, T. Romann, E. Lust, Electroanalytical Chemistry, accepted.

Electrochemistry of Hydrogen Peroxide and its Essential Role in the Oxygen Reduction Reaction

Ioannis Katsounaros,[a,b,c,d] Angel Cuesta,[e] Wolfgang B. Schneider,[f] Alexander A. Auer,[f] and Karl J.J. Mayrhofer[a]

[a] *Max-Planck-Institut für Eisenforschung, Department of Interface Chemistry and Surface Engineering (Germany)*
[b] *University of Illinois at Urbana-Champaign, Department of Chemistry (USA)*
[c] *Argonne National Laboratory, Materials Science Division (USA)*
[d] *Leiden University, Leiden Institute of Chemistry (The Netherlands)*
[e] *University of Aberdeen, Department of Chemistry (UK)*
[f] *Max-Planck-Institut für Chemische Energiekonversion, Department of Theoretical Chemistry (Germany)*
ikatsoun@illinois.edu; i.katsounaros@umail.leidenuniv.nl

In order to elucidate the participation of H_2O_2 in the ORR, it is essential to understand the electrochemistry of hydrogen peroxide under conditions relevant to the ORR. We have recently been investigating systematically the reactions of hydrogen peroxide reduction (PRR) and oxidation (POR) on single-crystalline [1], polycrystalline [2-4] and high-surface-area Pt [5] as well as on other metals, in the absence and presence of strongly adsorbing spectator species, which are known to have a tremendous impact on the ORR selectivity [6]. We show that the feasibility of the H_2O_2 reduction determines the selectivity of the ORR, so that eventually only an H_2O_2-mediated pathway that includes a competition between the dissociation and the desorption of the intermediate H_2O_2 is enough to explain and unify all the observations that have been made so far on the ORR selectivity.

Acknowledgments

I.K. acknowledges support by a Marie Curie International Outgoing Fellowship within the 7th European Community Framework Programme (Award IOF-327650).

References

1. I. Katsounaros, C. Vaz-Domínguez, K.J.J. Mayrhofer, C. Gutiérrez, A. Cuesta, (in preparation).
2. I. Katsounaros, W.B. Schneider, J.C. Meier, U. Benedikt, P.U. Biedermann, A.A. Auer, K.J.J. Mayrhofer, *Phys. Chem. Chem. Phys.* **14** (2012) 7384.
3. I. Katsounaros and K.J.J. Mayrhofer, *Chem. Commun.* **48** (2012) 6660.
4. I. Katsounaros, W.B. Schneider, J.C. Meier, U. Benedikt, P.U. Biedermann, A. Cuesta, A.A. Auer, K.J.J. Mayrhofer, *Phys. Chem. Chem. Phys.* **15** (2013) 8058.
5. I. Katsounaros, J.C. Meier, K.J.J. Mayrhofer, *Electrochim. Acta* **110** (2013) 790.
6. N.M. Marković and P.N. Ross, *Surf. Sci. Rep.* **45** (2002) 117.

Lithium Insertion into Titanium Dioxide: Electrochemistry, Raman Spectra and Isotope (Li, O) Labeling

Ladislav Kavan, Otakar Frank, Barbora Laskova, Marketa Zukalova
J. Heyrovsky Institute of Physical Chemistry, v.v.i. Academy of Sciences of the Czech Republic,
kavan@jh-inst.cas.cz

Analysis of cyclic voltammograms of Li insertion into TiO_2(B) and anatase provided information about capacitive contributions to overall charge of Li-storage. The enhancement of 30% was found in capacitive contributions (normalized to the total stored charges) in TiO_2(B) and anatase, in spite of ca. three times smaller surface area of the former. Different charging mechanism explained facilitated Li^+ insertion in TiO_2(B). The difference is caused mainly by pseudocapacitive Li-storage in the bulk TiO_2(B). Deconvolution of cyclic voltammograms also indicated different capacitive contributions of the two voltammetric peaks of TiO_2(B). These results provide novel insight into the Li-storage in TiO_2(B) and its difference from that in anatase. Six representative O-isotope labeled samples of titanium dioxide were synthesized: $Ti^{16}O_2$, $Ti^{17}O_2$ and $Ti^{18}O_2$, each in anatase and rutile forms. Furthermore, tiania labeled by Ti isotopes 46, 48 and 49 was also obtained. The found/calculated isotopic shifts in the Raman spectra elucidated various still open questions about the second-order Raman scattering in rutile, and about the overlapping features in the anatase spectrum. Electrochemical and chemical (with n-butyllithium) insertion of Li into TiO_2 (anatase) was studied by Raman spectroscopy and by in-situ Raman spectroelectrochemistry. Four isotopologue combinations in the system, viz. $^{6/7}Li_xTi^{16/18}O_2$ (with x being the insertion coefficient), were prepared and studied. The reversible transition of tetragonal/orthorhombic phases of anatase/Li-titanate was thus analyzed in detail. The combination of experimental and theoretical Raman frequencies with the corresponding isotopic shifts brings new inputs for the discussion of the electrochemical Li-insertion into TiO_2 (anatase).

Electrochemical Method for Extracting Non-Ferrous and Precious Metals from Refractory Materials Using Combined Reactions

Kenzhaliev B.K.
Kazakh-British Technical University
Tole by str. 59, of 251   Almaty, 050000
Republic of Kazakhstan
E-mail: bagdaulet_k@mail.ru

A method of extraction of non-ferrous and precious metals from complex and hard minerals using combined electrochemical reactions was developed. Getting the leaching reagent and dissolving metals was performed simultaneously. Served thiosulfate lixiviant solution and the other thio-compounds of sodium were used as leaching reagents. Composite sulfur-graphite electrode which contains 35 % of elemental sulfur (petrochemical waste production) used as sulfur source. As an initial solution for the combined reactions, the sodium hydroxide solution with a concentration of 0.1 - 2.0 M was used. Leaching was carried out at temperatures of 25 - 50 ° C. The current density is 150 - 400 A/m^2. The technogenic product with a chemical composition (%): Au (g/t) -1,12; Ag (g/t) - 33,61; Pb - 2,08; Fe - 5,1; Cu - 0,2; Zn - 0,34; S - 15.05 ; C sulf. - 14,45; Ca - 1.08; C - 6,9; C carb. - 4.7; SiO_2 - 30,22; Al_2O_3 - 1,4; $BaSO_4$ - 27,8; Sb - 0,007; Mn - 0.08 was used as one of the objects of the studies. With this method of leaching, extraction of gold reached 85 - 95 % for different process conditions. The rate of dissolution of gold increased sharply during the first 30 - 40 minutes of leaching. Analysis of the solutions showed complexity of chemical processes, occurring during the electrochemical extraction of metals from solutions. It should be emphasized that using of sulfur-graphite electrode as a cathode and an as anode leads to the same result. However, the use of sulfur-graphite electrode as a cathode leads to increasing selectivity of extraction of metals from mineral raw materials, which makes it possible to arrange the process for the production of solutions with a high concentration of individual metals in multiple steps. The method can significantly reduce the number of process steps in the chain from mineral raw materials to metal.

Graphene and Niobium Oxide/Graphene Supported Platinum-Cobalt Nanocomposites as Electrocatalysts for the Oxidation of Ethanol

Virginija Kepenienė, Jūratė Vaičiūnienė, Rokas Kondrotas, Vidas Pakštas, Loreta Tamašauskaitė-Tamašiūnaitė, E. Norkus
Center for Physical Sciences and Technology
A.Goštauto 9, LT-01108 Vilnius, Lithuania
virginalisk@gmail.com

In the present work, graphene and niobium oxide/graphene supported PtCo catalysts with the Pt:Co molar ratio 1:7 (denoted as PtCo/GR and $PtCoNb_2O_5$/GR) were fabricated by means of the rapid microwave heating method. The surface morphology, structure and composition of the synthesized catalysts were examined by transmission electron microscopy, X-ray diffraction and inductively coupled optical emission spectroscopy. The electrocatalytic activity of the synthesized catalysts towards the oxidation of ethanol in an alkaline medium was investigated by means of cyclic voltammetry and chronoamperometry.

It has been determined that the Pt loadings were 0.165 and 0.285 mg Pt cm^{-2} in the synthesized PtCo/GR and $PtCoNb_2O_5$/GR catalysts, respectively. For comparison, the bare Pt/GR catalyst with the Pt loading of 0.035 mg Pt cm^{-2} was used. The electroactive surface areas (ESAs) of the prepared catalysts were determined from the cyclic voltammograms of Pt/GR, PtCo/GR and $PtCoNb_2O_5$/GR catalysts recorded in a deaerated 0.5 M H_2SO_4 solution at a sweep rate of 50 mV s^{-1} by calculating the charge associated with the hydrogen adsorption.

It was found that Pt nanoparticles of about 1-3 nm in size were successively deposited onto the surface of graphene nanosheets. Pt nanoparticles were uniform and well dispersed on the surface of graphene. Ethanol oxidation current densities were found to be about 9 and 13 times higher at the PtCo/GR and $PtCoNb_2O_5$/GR catalysts, respectively, in comparison with those at the Pt/GR catalyst. Assuming ca. 1.5 and 1.8 times higher ESA of Pt/GR as compared with those of the PtCo/GR and $PtCoNb_2O_5$/GR catalysts, respectively, the ESA normalized ethanol oxidation current densities are ca. 14 and 21 times higher on the latter catalysts. The prepared catalysts seem to be a promising anodic material for direct ethanol fuel cells.

Acknowledgement

Postdoctoral fellowship is being funded by European Union Structural Funds project ”Postdoctoral Fellowship Implementation in Lithuania”.

Electrochemical Detection of Multi-target Therapeutics in Alzheimer’s disease

Anthony J. Veloso, Kagan Kerman
Department of Physical and Environmental Sciences
University of Toronto Scarborough
1265 Military Trail, Toronto, ON, Canada, M1C 1A4
**kagan.kerman@utoronto.ca*

Alzheimer's disease (AD) is an irreversible neurodegenerative dementia marked by substantial deterioration of memory and cognitive functions [1]. The Amyloid Cascade Hypothesis attributes the progression and onset of AD to an imbalance in amyloid-beta (Aβ), which aggregates to form neurotoxic supramolecular assemblies comprised of discrete structural conformations [1].

Herein, we characterized a small library of novel sym-triazine compounds designed to target multiple pathologies of AD, namely Aβ aggregation and acetylcholinesterase activity using various voltammetric techniques on screen-printed electrodes. In addition to these beneficial properties, sym-triazines were also found to significantly up-regulate differentiation in human neuronal cells, an effect that may play a pivotal role in counteracting neurodegeneration in early stages of AD [2-4].

We further demonstrated the development of an impedimetric immunosensor implementing conformation-specific antibodies to detect the formation of toxic fibrillar and oligomeric Aβ species *in vitro*. Binding was quantified as a function of charge transfer resistance and the efficacy of aggregation modulators to reduce the population of toxic conformations was evaluated. The methods presented highlight utility of electrochemical approaches as a powerful drug-screening tool for rapid characterization of modulated Aβ self-assembly processes [2-4].

References:

[1] D. J. Selkoe, Preventing Alzheimer’s disease, Science 337 (2012) 1488-1492.
[2] A. J. Veloso, K. Kerman, Advances in electrochemical detection for study of neurodegenerative disorders, Anal. Bioanal. Chem. 405 (2013) 5725-5741.
[3] A. J. Veloso, D. Dhar, A. M. Chow, B. Zhang, D. W. F. Tang, H. V. S. Ganesh, S. Mikhaylichenko, I. R. Brown, K. Kerman, Sym-triazines for directed multi-target modulation of cholinesterases and amyloid-beta in Alzheimer’s disease, ACS Chem. Neurosci. 4 (2013) 339-349.
[4] A. J. Veloso, A. M. Chow, D. Dhar, D. W. F. Tang, H. V. S. Ganesh, S. Mikhaylichenko, I. R. Brown, K. Kerman, Biological activity of sym-triazines with acetylcholine-like substitutions as multitarget modulators of Alzheimer’s disease, ACS Chem. Neurosci. 4 (2013) 924-929.

An Electrochemical Sensing Interface for Dengue Virus Detection

Nadiya Taha Darwish[a],Yatimah binti Alias[a] and Sook Mei Khor[a]*
[a]Department of Chemistry, Faculty of Science University of Malaya, 50603 Kuala Lumpur, MALAYSIA
**Corresponding author: Dr. Sook Mei Khor; E-mail: naomikhor@um.edu.my; Tel: +603-79677022/Ext: 2520; Fax: +603-79674195.*

Dengue fever is one of the deadly infection threatens the human kind. No efficient treatment or vaccine is available for preventing or treating the disease caused by Dengue virus. Therefore, diagnostic methods are necessary to detect the disease consistently and rapidly, and consequently treat Dengue virus infection in an early phase. The methods at present used to cultivate the virus or to identify the specific antibody are both unwieldy and time consuming. The Reverse transcription polymerase chain reaction (RT-PCR) method although fast for diagnosis in the viremia stage but RT-PCR protocols suffer from two limitations: a false negative result due to the variation of DENV serotypes and the absent of standard protocol. Biosensors and more specifically electrochemical biosensors have presented as potential alternatives to overcome all difficulties, because it is cost effective, robust, and able to detect very low concentration of analytes from different specimen mixtures and due to specific interaction to the analyte. In this study a sensing interface for dengue virus detection has been fabricated by modification of indium tin oxide (ITO) with diazonium salts. The electrochemical deposition was conducted by using electrochemical reduction method. The ITO sensing interfaces have been characterized *via* FeSEM, TEM, and FTIR. On the other hand, the electrochemical measurements were done by using two redox species $Ru(NH_3)_6Cl_3$ (1 mM) and $K_3Fe(CN)_6$ (1 mM). The well-constructed sensing interface gives promising platform for the development of biosensors for diagnosis of dengue virus which continues to be a major health problem in the tropical and subtropical regions of world.

Molecular Level Electrogenerated Chemiluminescence for Protein Analysis

Hasuck Kim[1,2] Hyo-Ju Seo,[1] Jeong-Wook Oh,[1] and Yang-Rae Kim,[1]
[1]Department of Chemistry, Seoul National University (SNU), Seoul 151-747, Korea
[2]Department of Energy Systems, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 711-873, Korea
E-mail: hasuckim@snu.ac.kr

Electrogenerated chemiluminescence (ECL) is the light-emitting process caused by the recombination of electrochemically generated redox species at electrodes in solution. ECL is a very promising tool for ultrasensitive biosensor because of combining advantages of electrochemical and optical techniques of portability and sensitivity, respectively. [1]

We have developed an ECL biosensor for protein based on $Ru(bpy)_3^{2+}$ doped silica nanoparticles (RSNPs). RSNPs exhibit a strong luminescent and highly photostable signal because it has a large number of luminophores encapsulated inside the rigid silica matrix. A sandwich type immunoassay system with RSNP was demonstrated with the various sizes of monodispersed RSNPs. In case of DNA sensing, for ultrasensitive detection of target DNA, the dendritic structure of RSNPs was constituted using the hybridization between the DNA on the former RSNPs and the complementary DNA on the additional RSNPs.

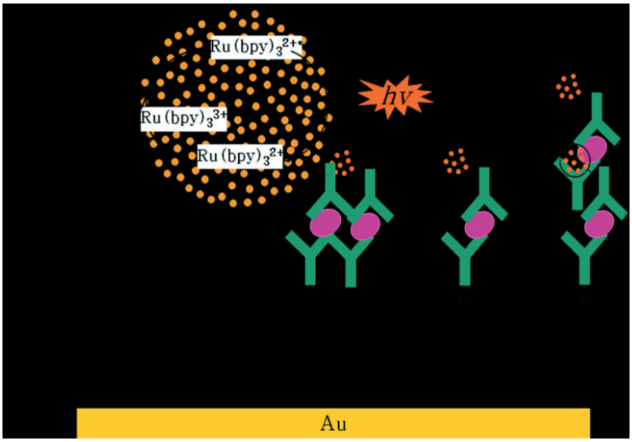


Fig. 1. Scheme of ECL-immunoassay based on $Ru(bpy)_3^{2+}$ doped silica nanoparticle.

[1] Ik-Soo Shin, Jae Il Kim, Tae-Hyun Kwon, Jong-In Hong, Jin-Kyu Lee, Hasuck Kim, J. Phys. Chem. C, 111(5), 2280-2286 (2007).
[2] Yang-Rae Kim, Hyo-Ju Seo, Jeong-Wook Oh, Hyunchang Lim, Tae Hyun Kim, Hasuck Kim, Electroanalysis, 25(4), 1056-1063 (2013).

Analytical Determination of the Reaction Products Resulted from Organics Electrooxidation on Various Nanomaterials

K. B. Kokoh
IC2MP, UMR-CNRS 7285, Université de Poitiers
4 rue Michel Brunet, B27, 86022 Poitiers Cedex France
boniface.kokoh@univ-poitiers.fr

Suitable analytical techniques can be combined with electrochemical experiments to provide specific information on the intermediates and/or final products of organics oxidation reactions. To understand and then propose, as realistic as possible, reaction mechanism of various investigated processes in the topical domain of fuel cells and renewable conversion and energy storage, different techniques such as chromatography, mass spectrometry, and *in situ* infrared spectroscopy were combined to follow the oxidative electrochemical transformation of alcohols, polyols and carbohydrates. As electrodes, Pt and Pd based nanoscale materials with different atomic compositions were synthesized from the bromide anion exchange (BAE) method [1,2].
The activity of the different nanomaterials was first evaluated in alkaline medium by CO stripping experiment. These electrochemical investigations coupled with *in situ* FTIR allowed determining that the adsorption modes of CO on Pd-based materials depend on the electronic structure of the particles. Afterwards, glycerol and glucose were used as fuels for their anodic electrooxidation on these catalysts. Compared to the monometallic electrodes, the bimetallic materials promote the reactivity of the molecules evidenced by the onset potential shifted towards lower values and the increase in the current densities. The coupling of analytical and spectroscopic techniques was helpful in the understanding of these organics electrooxidation.

Acknowledgments

The author gratefully acknowledges financial support from the French National Research Agency (ANR) through ChemBio-Energy program.

References

[1] Y. Holade, C. Morais, K. Servat, T.W. Napporn, K.B. Kokoh, ACS Catal., 3 (2013) 2403-2411.
[2] Y. Holade, C. Morais, S. Arrii-Clacens, K. Servat, T.W. Napporn, K.B. Kokoh, Electrocatalysis, 4 (2013) 167-178.

Enabling in-situ/in-operando soft X-ray spectroscopy for the catalytic and electrochemical reactions

Yi-Sheng Liu[1], Per-Ander Glans[1], and Jinghua Guo[1,2]*
[1]Advance Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
[2]Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA
*Presenting author: jguo@lbl.gov

Keywords: in-situ Soft X-ray Spectroscopy, Catalysis, Li-S Batteries

In many important energy systems such as energy conversion and energy storage, advanced materials and fundamental interfacial phenomena play crucial roles in device performance and functionality due to the complexity of material architecture, chemistry and interactions among constituents within. To understand and ultimately control the interfaces calls for in-situ/in-operando characterization tools in which soft X-ray spectroscopy offers many unique features. In this presentation, I will report the development of in-situ reaction cells for soft X-ray spectroscopic towards the studies of catalytic and electrochemical reactions in recent years. Some of the instrumentation design and experimental studies are given as the examples, e.g. the experiment for studying the chemical composition of graphene-oxide electrode materials in Li-S batteries [1-2], the Co NPs in catalytic reactions [3-5] and hole generation and dynamics of photoelectrochemical catalysis [6] under in-operando conditions.

Reference

[1] L. Ji, M. Rao, H. Zheng, L. Zhang, Y. Li, W. Duan, J.-H. Guo, E. J. Cairns, and Y. Zhang, ***J. Am. Chem. Soc.*** 2011, 133, 18522–18525.
[2] Liang Zhang, Liwen Ji, Per-Anders Glans, Yuegang Zhang, Junfa Zhu and Jinghua Guo, ***Phys. Chem. Chem. Phys.*** 2012, 14, 13670–13675.
[3] A. Tuxen, S. Carenco, M. Chintapalli, C. Chuang, C. Escudero, E. Pach, P. Jiang, F. Borondics, B. Beberwyck, A.P. Alivisatos, G. Thornton, W. Pong, J.-H. Guo, R. Perez, F. Besenbacher, and M. Salmeron, ***J. Am. Chem. Soc.*** 2013, 135, 2273-2278.
[4] V. Iablokov, S. K. Beaumont, S. Alayoglu, V. V. Pushkarev, C. Specht, **J.-H. Guo**, A. P. Alivisatos, N. Kruse, and G. A. Somorjai, ***Nano Lett.*** 2012, 12, 3091-3096
[5] F. Zheng, G. A. Somorjai, S. Alayoglu, J.-H. Guo, V. Pushkarev, Y. Li, P.-A. Glans, J.-L. Chen, ***Nano Lett.*** 2011, 11, 847-853
[6] A. Braun, K. Sivula, D. K. Bora, J. Zhu, L. Zhang, M. Gratzel, J.-H. Guo, and E. C. Constable, ***J. Phys. Chem. C*** 2012, 116, 16870-16875.

Electrochemistry of water at platinum – revisited

Marc T.M. Koper, Angela den Dunnen, Manuel Kolb, Janneke van der Niet,
Cansin Badan, Ludo Juurlink
Leiden Institute of Chemistry, Leiden University
PO Box 9502, 2300 RA Leiden, The Netherlands
m.koper@chem.leidenuniv.nl

The interaction and dissociation of water at well-defined platinum surfaces, as gleaned from blank voltammetry experiments on stepped platinum electrodes, is compared to modeling experiments in ultra-high-vacuum and detailed density functional theory calculations on the same platinum surfaces. It is shown that there is a clear distinction between (110) and (100) step sites, both in the adsorption of single species, as well as in the way mono- and multilayers of water interact with clean as well as hydrogen and oxygen-covered stepped platinum surfaces.

Electrochemical Studies of Protein Kinase Catalyzed Phosphorylations

Heinz-Bernhard Kraatz
University of Toronto Scarborough
1265 Military Trail, Toronto, M1C 1A4, Canada
bernie.kraatz@utoronto.ca

The detection of biological analytes or of biochemical processes by electrochemical methods requires in many cases the presence of a redox-active probe as part of the detection system. After a brief overview of recent bioelectroanalytical applications of modified surfaces, the focus of this seminar will be on the use of ferrocene-labeled ATP-derivatives for the study of protein kinase catalyzed transformations.

Briefly, during protein phosphorylation reactions, protein kinases catalyze the transfer of a phosphate group from ATP to a specific serine, threonine, or tyrosine residues of a protein [1]. We have recently introduced an organometallic conjugate of adenosine triphosphate bearing a ferrocene group at the γ-phosphate. Our studies show that protein kinases can use this molecule as a co-substrate thus transferring a redox active Fc group to a target. Here, results are presented for a range of kinases showing that this approach can be used to assess the activity of kinases and measure their inhibition by small molecules [2].

[1] S. Martić, H.-B. Kraatz, “Chemical biology toolkit for exploring protein kinase catalyzed phosphorylation reactions”, *Chem. Sci.* **2013**, *4*, 42-59.
[2] S. Martic, M. Gabriel, J. P. Turowec, D. W. Litchfield, H.-B. Kraatz, “Versatile Strategy for Biochemical, Electrochemical and Immunoarray Detection of Protein Phosphorylations”, *J. Am. Chem. Soc.* **2012**, *134*, 17036-17045.

Accurate Characterization of Ion Transport Properties in Lithium Ion Battery Electrolytes Using *In Situ* NMR.

Sergey A. Krachkovskiy, Allen D. Pauric, Athinthra Sethurajan, Bartosz Protas, and Gillian R. Goward
McMaster University, Hamilton, Ontario, Canada L8S 4L8
sergey.k@mcmaster.ca

The design and optimization of nonaqueous lithium ion battery electrolytes requires methods for measuring all relevant diffusional parameters, including diffusion constants and ionic transference numbers. An accurate characterization of the transport parameters is not a trivial task due to the fact that the values of self-diffusion coefficients of ions in an electrolyte solution depend strongly on the salt concentration. At the same time, the salt concentration inside a battery is neither stationary nor homogeneous during application of electric potential; rather, it is a function of current density, time and distance from the electrodes.

Herein we demonstrate the application of *in situ* slice-selective NMR diffusion measurements as a tool for the spatially and temporally resolved determination of lithium diffusivities in a conventional liquid electrolyte (1.0 M lithium bis(trifluoromethanesulfonyl)imide solution in propylene carbonate).[1] At the same time using *in situ* ^{7}Li NMR imaging it is possible to monitor the formation of the concentration gradient in lithium ion battery electrolyte upon the application of an electric field.[2] Our study unambiguously shows that the shape of the concentration gradient profile depends on both the transference number and the diffusivity values; as well as it is highly sensitive to the spatial and temporal inhomogeneity of the self-diffusion coefficients. Therefore using information about diffusivities obtained by slice-selective NMR measurement and combining it with Li concentration profile from NMR imaging one can employ computational methods of inverse modeling for accurate extraction of all required transport parameters.

All experiments were carried out using standard NMR equipment, and *in situ* electrochemical cell design, utilizing conventional 5mm NMR tube, previously reported by Hallberg et al.[3] So the proposed technique can be easily implemented in any modern R&D facility.

---

[1] Krachkovskiy, S.; Pauric, A.; Halalay, I.; Goward, G. *J. Phys. Chem. Lett.* **4** (2013), 3940-3944

[2] Klett, M.; Giesecke, M.; Nyman, A.; Hallberg, F.; Lindstrom, R. W.; Lindbergh, G.; Furo, I. *J. Am. Chem. Soc.* **134** (2012), 14654-14657.

[3] Hallberg, F.; Furo, I.; Yushmanov, P. V.; Stilbs, P. *J. Magn. Reson.* **192** (2008), 69-77

Enhancement of transport rates by incorporation of noble metal nanoparticles to iodine/iodide based ionic liquid charge relays

Pawel J. Kulesza, Iwona A. Rutkowska, Justyna Orlowska
Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland
pkulesza@chem.uw.edu.pl

The iodine/iodide redox system has so far been the most commonly and most successfully used as a charge relay (mediator) in Dye Sensitized Solar Cells (DSSCs). Recently, the iodide/iodine redox couple has been considered together with ionic liquids. The resulting redox-conducting electrolytes have several advantages: high conductivity, low vapor pressure, high iodide/iodine concentration and good electrochemical stability. Among disadvantages is their high viscosity if the charge transport mechanism is truly physical. If electron hoping between I^- and I is involved, its effectiveness would require fast dissociation of iodine (I_2), or triiodide (I_3^-), molecule. There is a need to develop means of inducing the I-I bond breaking to accelerate interfacial and bulk electron transfers. It has also been established that platinum (e.g. when deposited on the counter electrode of DSSC) catalyzes interfacial electron transfers in the iodine/iodide redox system. Surface chemistry data provide clear evidence that iodine (or iodides) chemisorb readily on platinum as monoatomic iodine. Strong interactions of Pt with iodine were reported and described; further, formation of the monolayer type coverages of strongly adsorbed monoatomic iodine together with weakly bound electroactive iodine/iodide was also postulated. In the present work, we explore the concept of three-dimensional distribution of nanostructured iodine-modified platinum (or other noble metal nanoparticles) within the electrolyte phase to enhance dynamics of iodine/iodide electron self-exchange as an attempt to develop a new generation of charge iodine-based relays for DSSC. The diagnostic experiments have been performed using the electroanalytical methodology developed for solid-state electrochemical measurements in the absence of external liquid supporting electrolyte. They have included measurements using the planar three-electrode cell utilizing an ultramicrodisk electrode and two-electrode type sandwich configuration. Regardless the mechanism, the charge propagation rates, when expressed in diffusional terms, have been found on 10^{-6} cm^2 s^{-1} level.

Acknowledgement: Collaboration Michael Graetzel, Shaik M. Zakeeruddin, and Magdalena Marszalek of EPFL, Lausanne, Switzerland is highly appreciated.

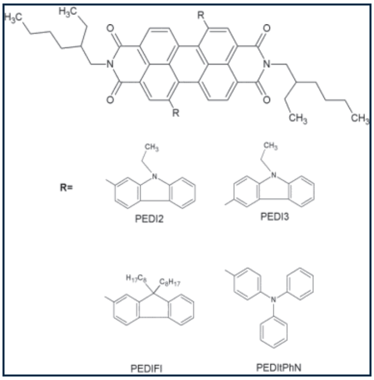
Electrochemistry and spectroelectrochemistry of bipolar perylene diimide derivatives

Mieczyslaw Lapkowski[1,2], Sandra Pluczyk[1], Renji R. Reghu[3], Juozas V. Grazulevicius[3]

[1]*Department of Chemistry, Silesian University of Technology, Gliwice, Poland*
[2] *Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, Zabrze, Poland*
[3]*Department of Organic Technology, Kaunas University of Technology, Kaunas, Lithuania*

Perylene diimide derivatives are class of interesting structures and one of the most important block of building n-doped materials. Additionally, the functionalization of the perylene diimide core with electron donating groups might lead to obtain ambipolar compounds, which are able to transport both kind of charge carriers: electrons and holes.

We report an electrochemical and spectroelectrochemical characteristic of four, bipolar perylene diimide derivatives (Fig. below).



Cyclic voltammetry (CV) of the investigated monomers show typical two-step reduction of the perylene diimide moiety. In the case of derivatives with carbazole units, the electrochemical oxidation of the studied compounds gives the corresponding polymer, which was deposited on the electrode. The resulting films were also examined by CV. Investigations indicate both: n-type and p-type doping of polymers. Moreover, analysis of redox processes of monomers and polymers were carried out using UV-Vis and ESR spectroelectrochemistry.

Field - Dipole Interactions in L-Cysteine-Thiolate Self Assembled at p- and n-GaAs(100) Electrodes

Valentina Lazarescu, Mirela Enache, Loredana Preda,
Mihai Anastasescu, Gianina Dobrescu,
Institute of Physical Chemistry "Ilie Murgulescu", Splaiul Independentei 202,
P.O. Box 12-194, RO-060041 Bucharest, Romania
Email: vlazarescu@icf.ro
Catalin Negrila, Mihail F. Lazarescu
National Institute of Material Physics, P.O. Box MG7, RO-77125 Bucharest,
Romania

Electrochemical impedance spectroscopy investigations on the L-cysteine-thiolate self-assembled monolayers spontaneously formed on p- and n-GaAs (100) electrodes brought evidence that the semiconductor doping exerts a complex control over their electrochemical behavior. The potential-induced reversible proton transfer found to occur within the L-cysteine-thiolate layer at p-doped semiconductor electrodes [1] during both the cathodic and the anodic potential scans appears only in the anodic scan at the n-doped ones.

The XPS data and the fractal analysis of the AFM images taken before and after the EIS measurements reveled that the observed difference originates in the field – dipole interactions operating distinctively in the L-cysteine-thiolate layer formed at p- and n-doped semiconducting substrates. The interaction of this small but highly polar molecule with the electrostatic field driven by the diffuse distribution of the excess charge in the semiconductor subsurface region both in equilibrium and under polarization conditions turned out to play a key role in determining the optimal orientation of the two polar groups which seems to be a perquisite for the potential-induced internal proton transfer.

References

[1]. V. Lazarescu, M. Enache, M. Anastasescu, G. Dobrescu, C. Negrila, M.F. Lazarescu, Electrochimica Acta (in Press, Accepted Manuscript)

Control of Magnetism at the electrode/electrolyte interface

K. Leistner, L. Reichel, K. Duschek, H. Schlörb, S. Fähler, L. Schultz
IFW Dresden
P.O. Box 270116, D-01171 Dresden
k.leistner@ifw-dresden.de

Reversible control of magnetism in nano- and micromagnets by an external parameter is of strong interest for magnetic data storage and microelectromechanical systems. At the electrode/electrolyte interface, the electrode surface and thus its magnetism can be modified via an external voltage by a multitude of electrode processes – double layer charging, ad- and desorption and faradaic reactions. In ultrathin FePt [1] and CoPt films, e.g., double layer charging leads to strong changes in magnetic coercivity due to changes in the electronic band structure at the metal surface. In case that charge is not only accumulated, but transferred at the interface, microstructure and phase changes result - exhibiting an even stronger effect on magnetism. Especially oxide oxidation and reduction reactions, known also from supercapacitors and batteries, can be reversible. For this purpose reversible iron oxide reduction and oxidation have been realized in Li based electrolytes [2] and in KOH. Magnetic measurements during electrochemical polarization were conducted in a home-made in-situ Hall cell. For Fe and FePt/Fe composite films large reversible changes of saturation magnetization (4-13%) and magnetic anisotropy (20%) were achieved [3]. This concept not only allows to research voltage dependent magnetism at the nanoscale, but also to monitor the first stages of electrochemical deposition of magnetic materials.

[1] *Weisheit et al. Science 315 (2007) 349,* [2] *Leistner et al. Phys. Rev. B 87 (2013) 224411,* [3] *Leistner et al. Electrochim. Acta 81 (2012) 330*

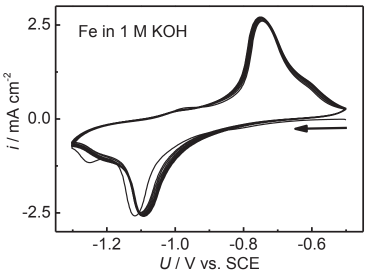


Fig. 1: Fe in KOH showing reversibility

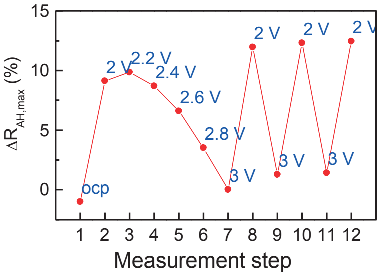


Fig. 2: 13% Change of saturation magnetization of FePt/Fe in $LiPF_6$ in DMC/EC [2]

Voltage Induced Changes in the Structure of the Cholera Toxin B Subunit Bound to a Model Membrane

J. Jay Leitch[†], Christa L. Brosseau[‡], Kyrylo Bessonov[†], Sharon G. Roscoe[#],
John R. Dutcher[†], Jacek Lipkowski[†]
[†]*University of Guelph, Guelph, ON, CA, N1G 2W1*
[‡]*St. Mary's University, Halifax, NS, CA, B3H 3C3*
[#]*Acadia University, Wolfville, NS, CA, B4P 2R6*
leitchj@uoguelph.ca

The biochemistry of cholera toxin infections has been extensively studied over the years, however, the mechanism by which the toxin is able to transport across the plasma membrane remains elusive. In addition, it is well-known that both the binding and translocation of the cholera toxin is dependent on membrane lipid rafts that are rich in cholesterol and GM1 phospholipids.[1] The binding subunit of the cholera toxin behaves as a voltage-gated ion channel, which preferentially transports anions, when bound to the surface of a cell membrane.[2] Therefore, in order to gain more insight into the protein-membrane interactions that lead to cell infection, model membranes can be employed to study the electric field-induced structural changes to the membrane bound toxin.

Model biological membranes composed of DMPC, cholesterol and cholera toxin B (CTB) bound-GM1, were deposited on the surface of a gold(111) electrode using a combination of the Langmuir-Blodgett and Langmuir-Schaefar deposition. Polarization modulation infrared reflection absorption spectroscopy was employed to examine the changes in the structure and orientation of the phospholipid molecules due to the binding of CTB to the GM1 receptors. The IR spectra suggest that cholera toxin causes an increase in the average tilt angle of the lipid tails when binding to GM1, however, the overall fluidity of the membrane remains constant. In addition, the structure and orientation of the phospholipid molecules are potential-independent for potentials ranging from 0.4 to −0.8 V.

In contrast, the CTB subunit displayed a significant voltage-dependent behaviour. The orientation of the α-helical residues located within the central pore of the cholera toxin protein showed an increase in the average tilt angle from 15^o to 35^o when the voltage was decreased from 0.2 to −0.2 V. This change in the tilt angle of the α-helices corresponds to the voltage-gated opening/ closing of the helical pore. From these calculations, the width of the helical pore, at the more positive potentials, has a radius of 2.5 nm. Therefore, the CTB subunit may allow for translocation of the A-subunit when the channel is in the open state.

(1) Lencer, W.; Saslowsky, D. *Biochim. Biophys. Acta.* **2005**, *1746*, 314−321
(2) Krasilnikov, O. V.; Muratkhodjaev, J. N.; Voronov, S. E.; Yezepchuk, Y. V. *Biochim. Biophys. Acta.* **1991**, *1067*, 166−170.

Development of Doped and Coated Cathodes for Highly Stable Li-sulfur Batteries

Xia Li[1], Jian Liu[1], Xifei Li[1], Mohammad Banis[1], Biqiong Wang[1], Ruying Li[1], Mei Cai [2]and Andy X. Sun[1]*
[1]*Department of Mechanical and Materials Engineering,*
University of Western Ontario, London, ON, Canada N6A5B9
[2]General Motors R&D Center, Warren, 48090-9055, MI, USA
**Corresponding author: xsun@eng.uwo.*

Introduction

Li-sulfur battery is considered as the next generation of high energetic batteries due to the high theoretical capacity of sulfur [1, 2]. However, it is still hindered by the insulating sulfur and shuttle effect derived from dissolved polysulfide species in practical. Based on these issues, we developed two strategies to address them. One is to develop N-doped to carbon cathode to enhance the interaction and the other is to apply atomic layer deposition coating.

Results and Discussion

In the first part, different heteroatoms involved (nitrogen, oxygen, and pristine) porous carbon blacks on sulfur cathodes are evaluated. It confirmed that nitrogen involved carbon showed excellent electrochemical performance on Li-S battery. Further, detailed evidence on heteroatoms effect and scheme of discharge product depositing process are shown in Fig.1 (a).

ALD coating has been widely applied in Li-ion batteries [3]. In the second part, we report ALD Al_2O_3 on sulfur cathodes. Improved cycling stability and columbic efficiency of batteries was showed in Fig.1 (b). Further, mechanism of ALD coating layers with different thicknesses was studied in this part.

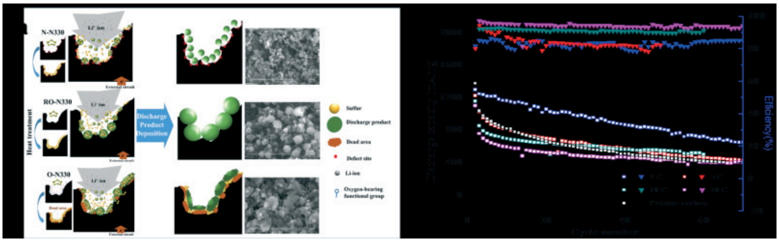


Fig. 1. (a) Scheme of discharge product depositing process of sulfur cathode with heteroatom involved carbon blacks as host, (b) Cycle performance of sulfur cathodes with different ALD coating layers

Reference

[1] D. Bresser, S. Passerini, B. Scrosati, Chemical communications, 49 (2013) 10545-10562.
[2] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.M. Tarascon, Nature materials, 11 (2012) 19-29.
[3] X. Meng, X.Q. Yang, X. Sun, Advanced materials, 24 (2012) 3589-3615.

New Insight into Electrocatalysis for Direct Alcohol Fuel Cells at Electronic, Atomic and Molecular Levels

Wen-Feng Lin
Centre for the Theory and Application of Catalysis, School of Chemistry & Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, UK
w.lin@qub.ac.uk

Direct Alcohol Fuel Cells (DAFCs) as an emerging clean energy technology are very attractive as power sources for mobile and portable applications. Nonetheless, on the basic research side, a significant challenge is to gain a fundamental understanding of fuel cell catalyst structures and their corresponding catalytic reaction mechanisms. The fundamental studies can provide a platform not only for understanding catalyst performance but also for exploring the structure-activity relationship at atomic and molecular levels; and ultimately for rationally designing new improved catalysts. On application side, innovation in fuel cell stack design is crucial for achieving high power density and developing efficient fuel cell systems as a versatile clean energy technology.

The main part of this talk is on fundamental electrocatalysis studies. The surface structure and reactivity of a series of well-defined model catalysts and the nanostructured and novel supported practical fuel cell catalysts, towards the adsorption and electro-oxidation of a range of small organic fuel molecules in various electrolyte solutions, at both room temperature and elevated temperatures, have been studied by combined *in-situ* electrochemical FTIR spectroscopy, *ex-situ* electron diffraction and Auger electron spectroscopy, and Density Functional Theory calculations. New insights into the surface structures and electrocatalysis have been obtained at electronic, atomic and molecular levels.

An additional part of this talk is on fit-for-purpose fuel cell system development. Novel electrode structure, MEA (membrane-electrode-assembly), single cell and stack design and fabrication will be reported briefly.

Acknowledgments: This work was supported by the UK EPSRC (EP/I013229/1) and International Science & Technology Cooperation Program of China (2010DFB63680).

Electroreduction and dimer formation of Fischer Cr(0)-aminocarbene complexes with heterocyclic substituents.

Jiří Ludvík[a], Radka Metelková[a,b], Miroslav Polášek[a], Irena Hoskovcová[b]
[a]*J. Heyrovský Institute of Physical Chemistry, Acad. of Science of the Czech Rep.,,*
Dolejškova 3, 182 23 Prague 8, Czech Republic, e-mail: jiri.ludvik@jh-inst.cas.cz
[b]*Department of Inorganic Chemistry, Institute of Chemical Technology Prague,*
Technická 5, 166 28 Prague 6, Czech Republic

Fischer type aminocarbene complexes are useful not only as precursors in organic synthesis but they are also promising redox catalysts. Molecular electrochemistry represents a suitable approach to this research. Combination with UV-vis spectroelectrochemistry, preparative electrolysis, MS, and NMR was used. Reduction mechanism was investigated on a series of chromium aminocarbene complexes (Fig. 1) substituted by three types of five-membered heterocycles attached in positions 2 and 3.

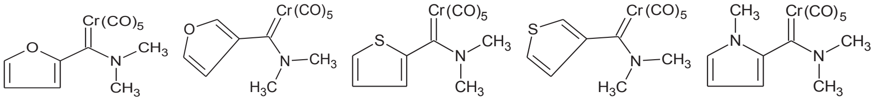


Figure 1*: Structure of the studied carbene complexes series.*

The nature of the heterocycle, as well as the influence of the site, where the heterocycle is attached to the carbene moiety has important consequences on their redox behaviour [1]. Due to the more extended π-sytem, the 2-hetaryl carbenes are reduced less negatively. The final product is generated by "dimerization" of reduced carbene carbon of the original molecule. The resulting dimer has four bonding isomers. NMR spectroscopy and MS were used for identification of the products. As the main product a symmetrical dimeric derivative was identified [2]

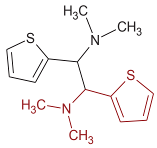


Figure 2*: Structure of the main product.*

Acknowledgement: This work was supported by grant: GAČR P206/11/0727

References:

[1] Metelková R, Kvapilová H, Hoskovcová I, Tobrman T, Ludvík J, Electrochim. Acta (2012), 82, 470-477.
[2] Metelková R. *et al.* – to be published

New approach of data mining from the complex impedance plane: parameters you have always wanted to have

J.M. Macak*, D. Patil, M.Fraenkl, V. Zima, K. Shimakawa, T. Wagner
Department of General and Inorganic Chemistry
Faculty of Chemical Technology, University of Pardubice
Nam. Cs. Legii 565, 530 02 Pardubice, Czech Republic
**jan.macak@upce.cz*

Conventional analysis of data recorded using the Electrochemical Impedance Spectroscopy (EIS) is a relatively simple procedure from the mathematical point of view. It involves an elucidation of electrode processes to derive their characteristic parameters. The EIS represents a quick visualization tool being still a very sensitive technique. However, it has a number of disadvantages too. Often, the interpretation of EIS data using equivalent circuits is quite difficult due to a tedious search for a good fitting correlation [1]. Moreover, results do not give information about number of moving ions (cations or anions), hopping time etc. Knowledge and consideration of these parameters would be very helpful in many electrochemistry-related fields, such as for instance in the development of solid state batteries and in the semiconductor field. Being unhappy with these drawbacks and limitations of the conventional data analysis method, we recently developed a new approach [1] in which the Z_1 - Z_2 complex impedance plane (where Z_1 and Z_2 are the real and imaginary parts of the impedance of materials) has been analyzed, based on Dyre's random-walk theory. Through this approach we have obtained from EIS data (that are measured anyway), a new set of physical parameters, yet unseen and unmined: i) the diffusion coefficient D and ii) the number of moving ions $N_{\text{ions,}}$ both parameters further distinguishable in the bulk region of the sample as well as at the interface. The presentation will explain in detail our recently developed approach that has the potential to find a widespread use in various electrochemical fields, such as in batteries, solar cells, fuel cells and semiconductor industry in general. The presentation will show, how helpful this approach can be to understand the electrode polarization as well as the ionic transport mechanism in various conductors. In particular, we will discuss in detail recent results achieved on various materials, including selected ionic conductors [2], silicons and TiO_2.

1.D. D. Macdonald, Transient Techniques in Electrochemistry, Springer US, 1977.
2. D.S. Patik, K. Shimakawa, V. Zima, J. Macak, and T. Wagner, J. Appl. Phys. 113 (2013) 143705.

Surface X-ray Scattering Studies of Electrochemical Growth at Solid-liquid and Liquid-liquid Interfaces

Olaf M. Magnussen
Institute for Experimental and Applied Physics,
Christian-Albrechts-University Kiel, 24098 Kiel, Germany
magnussen@physik.uni-kiel.de

Electrodeposition and -dissolution processes are of substantial importance for current and future technological applications, e.g. the fabrication of micro- or nanostructures and reactions in electrochemical energy storage. It thus is essential to better understand the atomic-scale growth as well as the underlying elementary interface processes. As shown here, surface X-ray scattering methods offer unique opportunities for studying electrochemical growth *in situ* on the atomic scale.

Firstly, the possibilities for obtaining detailed insight into the potential dependent growth behavior will be illustrated for the case of the homoepitaxial electrochemical deposition and dissolution of Au and Cu in Cl-containing electrolyte [1-3]. Using fast area detectors, these irreversible processes can be studied at growth rates up to several ten monolayers per second, i.e., under technologically relevant conditions. Characteristic differences between the growth behavior of Au and Cu reveal the pronounced influence of coadsorbed Cl on surface transport, which can even induce an inverted potential-dependence [3]. Furthermore, *in situ* GISAXS studies provide data on the temporal evolution of the nanoscale growth morphology, as demonstrated by studies of Au(001) deposition in the 3D growth regime.

Secondly, X-ray scattering techniques are unique in allowing atomic-scale studies of liquid-liquid interfaces [4]. As an example, reflectivity and grazing incidence data for crystal growth on a liquid mercury electrode in lead-containing solution will be shown. This study reveals a complex behavior, involving an ultrathin precursor layer which controls the orientation of the subsequent 3D crystallization process.

[1] K. Krug, J. Stettner, and O. M. Magnussen, *Phys.Rev.Lett.* **96**, 246101 (2006).
[2] F. Golks, K. Krug, Y. Gründer, J. Zegenhagen, J. Stettner, O. M. Magnussen, *J. Am. Chem. Soc.* **133**, 3772 (2011).
[3] F. Golks, J. Stettner, Y. Gründer, K. Krug, J. Zegenhagen, O.M. Magnussen, *Phys. Rev. Lett.* **108**, 256101 (2012).
[4] A. Elsen, B. M. Murphy, B. M. Ocko, L. Tamam, M. Deutsch, I. Kuzmenko, O. M. Magnussen, *Phys. Rev. Lett.*, **104**, 105501 (2010).
[5] A. Elsen, S. Festersen, B. Runge, C.T. Koops, B. M. Ocko, M. Deutsch, O. Seeck, B. M. Murphy, O. M. Magnussen, *Proc. Nat. Acad. Sci.* **110**, 6663 (2013).

Electrochemical Detection of Tau-tau Protein Binding on Gold Surfaces

Sanela Martic,*$ Jose O. E. Villanueva, Hanna Trezeciakiewicz
Oakland University
Department of Chemistry, Rochester, MI, USA, 48309
martic@oakland.edu

Tau protein self-assembles into oligomers and filaments causing neurodegenerative diseases, such as Alzheimer's Disease [1]. Despite the well characterized morphologies of insoluble tau filaments, the mechanism of their formation and the conformational protein changes are less understood. Here we describe the use of electrochemical impedance spectroscopy, in combination with ellipsometry and contact angle measurements, for detection of conformational changes, tau-tau binding, and formation of a protein dimer. The effects of protein concentration, pH, and surface modifications on tau-tau binding will be discussed.

[1] a) M. Goedert, A. Klug, R. A. Crowther, Tau protein, th apaired helical filament and Alzheimer's Disease, J. Alzheimers Dis. 9 (2006) 195-207. b) M. von Bergen, P. Friedhoff, J. Biernat, J. Heberle, E. M. Mandelkow, E. Mandelkow, Assembly of tau protein into Alzheimer pared helical filaments depends on a local sequence motif ((306)VQIVYK(311)) forming beta structure, Proc. Natl. Acad. Sci. U.S.A. 97 (2000) 5129-5134.

Modulation of Charge Transfer Across Double Stranded DNA by Site-Specific Incorporation of Copper bis-Phenanthroline Complexes

Philippe Dauphin Ducharme[‡], Fiora Rosati[‡], Andrea Greschner, A. Dowine Dea Bruijn, Danielle Salvatore, Violeta Toader, Kai Lin Lau,
Janine Mauzeroll* and Hanadi Sleiman*
McGill University,
Department of Chemistry,
801 Sherbrooke Street West,
Montreal, Canada, H3A 0B8
Janine.Mauzeroll@mcgill.ca

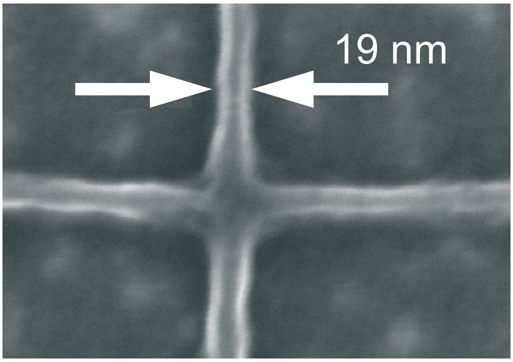
We demonstrate through electrochemical measurements that site-specifically incorporated transition metals are electronically coupled to the DNA base stack. For this, we use a modular approach to build DNA duplexes containing one or two $\mathrm{Cu^{I}}$ centres coordinated to 2,9-bis-1,10-diphenyl phenanthroline (dpp) ligands. This allows the fine modulation of charge mediation without altering DNA structure. We find that an immobilized DNA duplex labeled with one copper center can mediate the charge involved in $\mathrm{Cu^{I}}$ to $\mathrm{Cu^{II}}$ oxidation. When labeled with two copper centers, the anodic current shows a two-fold increase, even though the distal copper is *ca*. 20 nm away from the electrode. Introducing two mismatches in the DNA duplexes results in a significant (e.g., 82%) reduction of the current. To our knowledge, this is the first electrochemical demonstration of DNA-mediated charge transport in a non-intercalating metal-DNA conjugate, and it allows these copper phenanthroline units to open charge conduction pathways within DNA nanostructures.[1]

[1] S. Liu, G. H. Clever, Y. Takezawa, M. Kaneko, K. Tanaka, X. Guo, M. Shionoya, *Angew. Chem. Int. Ed.* **2011**, *50*, 8886-8890.

Fabrication and applications of carbon nano-band electrodes

Mark T. McDermott, Rongbing Du
Department of Chemistry and National Institute for Nanotechnology
University of Alberta
Edmonton, Alberta
mark.mcdermott@ualberta.ca

Our group has developed a method to fabricate nanometer scale carbon electrodes through a combination of electron beam lithography (EBL) and pyrolysis of the resulting pattern in the resist material. The resulting structures have a graphitic character with controllable size, shape and position and function well as nano-electrodes. For example, the figure below is an SEM image of a cross-shaped carbon structure with a width of 19 nm. A detailed voltammetric investigation of nanoband electrodes of various widths will be presented with comparisons to nanoband theory. We have also studied metal electrodeposition at these carbon nanostrutures. The size and morphology of the deposited Au particles depends greatly on the substrate. On the nanoband electrodes, the Au particles exhibit dendridic morphology with diameters around 100 nm. Their size and surface area are much larger than those electrodeposited on the carbon film electrode under the same conditions. We have subsequently studied the surface enhanced Raman spectroscopy (SERS) properties of the gold deposited on the nanobands. We observe a high enhancement in Raman intensity for a molecular layer on the nanoband supported gold relative to particles deposited on the macroscale electrode. The mechanism of gold deposition onto nanoband electrodes will be discussed in terms of mass transport phenomena.



An All-Inorganic Responsive Surface: Reversible Electrochemical Contact Angle Switching of Hexagonal Boron Nitride Nanomesh

Stijn F.L. Mertens,[a,b] Adrian Hemmi,[c] Stefan Muff,[c] Rafael Küng,[c]
Steven De Feyter,[a] Jürg Osterwalder,[c] Thomas Greber[c,]*
[a] *Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium,* [b] *Institut für Angewandte Physik, TU Wien, Wiedner Hauptstraße 8-10/E134, 1040 Wien, Austria,* [c] *Physik-Institut, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland*
greber@physik.uzh.ch

The nanomesh superstructure formed by a monolayer of hexagonal boron nitride (*h*-BN, isoelectronic with graphene) on Rh(111) holds great promise for supramolecular ordering [1] and other nanoscale phenomena. In this work, we have studied the dynamic contact angle at the interface between *h*-BN/Rh(111) and an electrolyte as a function of the electrochemical potential. We observe a strong effect on the contact angle in the potential region where hydrogen adsorption occurs on Rh(111) [2]. Supported by *in situ* STM observations and thermal desorption spectroscopy, we propose that this macroscopic effect is caused by nanotexture switching within the 3 nm unit cell of the nanomesh, as hydrogen intercalation flattens the sp^2 hybridised boron nitride layer [3]. The changes in dynamic contact angle of the electrolyte were observed *in situ*, using a 3-electrode setup, and were fully reversible under electrochemical control. To our knowledge, this system probably represents the first all-inorganic responsive surface.

[1] Berner *et al*. Angew. Chem. Int. Ed. **2007**, 46, 5115.
[2] Widmer *et al.* Electrochem. Commun. **2007**, 9, 2484.
[3] Brugger *et al*. Angew. Chem. Int. Ed. **2010**, 49, 6120.

Electrochemistry of Ferrocene Based Charge-Transfer Chromophores Containing Various Bridging Units

T. Mikysek[a], J. Ludvík[b], and K. Vytřas[a]
[a] *Department of Analytical Chemistry, University of Pardubice, Studentská 573,*
CZ-53210 Pardubice, Czech Republic.
[b] *J. Heyrovsky Institute of Physical Chemistry ASCR, v.v.i., Dolejškova 3,*
CZ-182 23 Prague 8, Czech Republic.
e-mail: tomas.mikysek@upce.cz

Recently, two series of new ferrocene derivatives of the "push-pull" type were synthesized and basic characterisation has been performed [1,2]. Both series contained ferrocene group playing role of donor and NO_2 group (serie 1) or 4,5-dicyanoimidazole (serie 2) acting as an acceptor. Moreover in both series the donor and acceptor group were connected via various bridging units (thienylene and phenylene) of different length. These derivatives were selected in order to characterise them electrochemically using polarography, cyclic voltammetry (CV) and rotating-disc voltammetry (RDV) at platinum electrode in non-aqueous media (acetonitrile, N,N-dimethylformamide). From the CV measurements resulted that there are several redox processes. The attention has been paid to the first oxidation and reduction. In both series the first oxidation process as well as the first reduction seems to be one electron and diffusion controlled. The influence of different linker has been also studied and from CV has been pointed out that length of π-conjugated spacer plays an important role in electrochemical behaviour. Next step in evaluation of the CV data was determination of HOMO-LUMO gap which helps in selection of some derivatives for further experiments. Based on this preliminary characterisations it will be possible to further tune the structure for use of the derivatives in electronic or NLO applications.

Acknowledgement

The Ministry of Education, Youth and Sports of the Czech Republic, Project CZ.1.07/2.3.00/30.0021 "Enhancement of R&D Pools of Excellence at the University of Pardubice", financially supported this work. The authors thank the team of Assoc. Prof. Filip Bureš for synthesis of examined organic compounds.

References

[1] J. Kulhánek, F. Bureš, W. Kuznik, I. V. Kityk T. Mikysek, A. Růžička: *Chem. Asian J.* **8** (2013) 465 .

[2] J. Kulhánek, F. Bureš, J.Opršal, W. Kuznik, T. Mikysek, A. Růžička: *Asian J. Org. Chem.* **2** (2013) 422 .

Microstructural Design of Nanoarchitectures for Energy Storage

David Mitlin
[a]*Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB*
dmitlin@ualberta.ca

Nanostructured materials hold great promise for energy storage applications, possessing both obvious intrinsic advantages and obvious intrinsic disadvantages. These systems have nanometer-scale diffusion distances and extremely high surface-to-volume ratios. On the up side this allows for exquisite kinetics, potentially altered thermodynamics, and near theoretical electrochemical activities. On the down side such systems often display markedly accelerated rates of microstructural degradation, and are prone to extensive parasitic side reactions. The theme of this presentation is the use of microstructural control to extend the favorable attributes of “Nano”, and minimize the undesirable ones, in relation to lithium ion battery (LIB) and electrochemical supercapacitor electrode materials. In this talk I will cover several examples where proper microstructural design provides substantial improvements: A) The use of nanoscale coatings to more than double the cycling capacity retention and achieve near 100% coulombic efficiency of Si nanowire LIB anodes; B) Creating a true nanocomposite consisting of an interconenected graphene backbone supporting oxide nanocrystals, which allows for excellent energy-power characteristics even with commercial-level mass loadings; C) Converting a common livestock biowaste, in the form of chicken eggshell membranes and inedible egg whites, to electrodes with some of the highest specific capacitances and charge storage capacities ever reported in literature for any carbon; D) Creating carbons with electrochemical performance on par or even better than graphene from the bark of agricultural hemp. In all cases I will detail the key processing – microstructure features that transform the performance of these materials from mundane to remarkable.

Preparation and Characterization of Nanostructured Electrode Materials

Sylvie Morin, Sreena R. Thekoot, Muhammad Nazari, Antoine Dumont, Maryam Hariri and Ali Sepehri Fard
Department of Chemistry, York University
CB 124, 4700 Keele Street, Toronto, ON M3J 1P3
smorin@yorku.ca

Much effort has been made recently to address the need for electrode materials with specific morphology and properties. In this presentation, we will report on preparations, characterization and specific properties of mesoporous doped titanium dioxide as solar cell anodes and copper cobalt oxide spinels as transparent electrodes for solar cell applications.

The doped TiO_2 is prepared by sol gel method. While the materials structure does not differ significantly from the undoped material, Raman imaging points to the formation of dopant rich particles. For $Cu_xCo_{3-x}O_4$, two different methods of preparation were chosen - coprecipitation and thermal decomposition. The films were tested for their conductivity and electrocatalytic properties in correlation to their composition and structure. Figure 1 a) and b) show the morphologies of two spinels of similar composition but prepared using thermal decomposition and co-precipitation methods, respectively. The structures were determined by x-ray diffraction (data not shown). Control of materials structure/property will also be discussed.

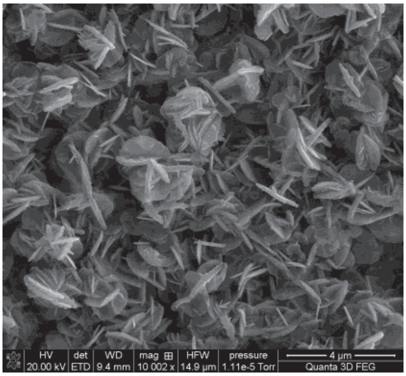


Fig. 1 a) SEM image of a $CuCo_2O_4$ film prepared by thermal decomposition on glass.

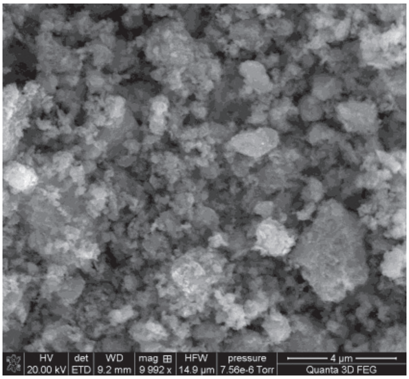


Fig. 1 b) SEM image of a $CuCo_2O_4$ powder prepared by co-precipitation method.

Fast Redox Communication at Organometallic Carbon-rich Ruthenium Complexes Self-Assembled Monolayers

Andrea Mulas, Yves-Marie Hervault, Xiaoyan He, Lucie Norel, Stéphane Rigaut
and Corinne Lagrost
Institut des Sciences Chimiques de Rennes UMR CNRS n°6226
Université de Rennes 1 -Campus de Beaulieu, F-35042 Rennes Cedex, France
andrea.mulas@univ-rennes1.fr

Carbon-rich ruthenium complexes are used to form Self-Assembled Monolayers (SAMs) onto gold surfaces. These organometallic compounds promote a strong electronic coupling between the metal centers and the conjugated organic ligands, useful to achieve functional molecules.[1,2] They also exhibit fast electron transfer rates and low oxidation potentials, making them attractive system for integration in devices as memory elements. In that respect, electron transfer kinetics inside the SAMs was examined using fast cyclic voltammetry. The influences of i) the nature of the anchoring groups (thiol, carbodithioate or isocyanide), ii) the length of the bridging unit used to space redox centers and anchoring groups and iii) the dilution as mixed SAMs with non electroactive thiols were examined to rationalize and optimize the interfacial electron transfer kinetics. An additional level of sophistication could be reached from association of dithienylethene (DTE) photochromic units with these organometallic complexes. These materials display unique electrochemical properties, with multicolor electrochromism, photo/electro tuning of electronic communication allowing appealing modulation of the redox communication at the SAMs.[3]

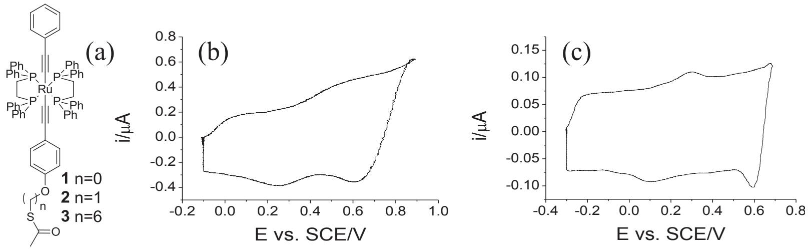


*Figure 1. a) Examples of complexes under study; ume CVs at 10 kV s^{-1} in CH_2Cl_2 containing 0.2 M $TBAPF_6$ of (b) SAMs of **3**; (c) mixed SAM of **3** and hexanethiol.*

(1) Olivier, C.; Costuas, K.; Choua, S.; Maurel, V.; Turek, P.; Saillard, J.-Y.; Touchard, D.; Rigaut, S. *J. Am. Chem. Soc.* **2010**, *130*, 5638-5651

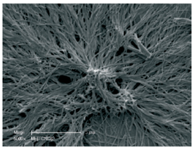
(2) Meng, F.; Hervault, Y.-M.; Shao, Q.; Hu, B.; Norel, L.; Rigaut, S.; Chen, X. *Nat. Commun.* DOI: 10.1038/ncomms4023

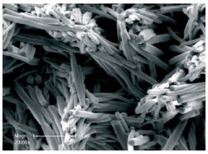
(3) Liu, Y.; Lagrost, C.; Costuas, K.; Tchouar, N.; Bozec, H.; Rigaut, S., *Chem. Commun.* **2008**, 6117-6119.

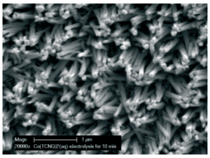
Synthesis, Characterization, and Utilization of Metal-TCNQ Nanostructured Materials in Graphene-Based Flexible Energy Storage Devices

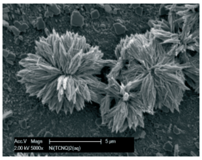
Ayman Nafady and Alan M Bond
Chemistry Department, King Saud University, Riyadh, Saudi Arabia
anafady@ksu.edu.sa

TCNQ-based molecular materials have potential applications in diverse areas such as, data and energy storage devices, organic field-effect transistors and electrochromic and magnetic devices. In this presentation, facile electrochemical and photochemical approaches for the synthesis, characterization, and fabrication of morphology-tunable semiconducting/magnetic $M[TCNQ]_2$-based materials (M = Mn, Fe, Co, Ni, Zn, and Cd) onto conducting (Pt, Au, GC, Gr), semiconducting (ITO) and insulating (glass, plastic) surfaces will be discussed. Characterization of these $M[TCNQ]_2$-based materials via wide range of spectroscopic (IR, Raman), microscopic (optical, SEM, EDX), as well as conventional and synchrotron-based XRD techniques will be presented. This study provides an easy access for controlling the morphology and crystals size of the electrochemically generated $M[TCNQ]_2(H_2O)_2$ molecular materials to suit their desired applications.


$Mn[TCNQ]_2(H_2O)_2$


$Fe[TCNQ]_2(H_2O)_2$


$Co[TCNQ]_2(H_2O)_2$


$Ni[TCNQ]_2(H_2O)_2$

References:
(1) Nafady, A.; O'Mullane, A. P.; Bond, A. M.; Neufeld, A. K. *Chem. Mater.* **2006**, *18*, 4375.
(2) Nafady, A., Bond, A. M. et al *J. Am. Chem. Soc*. **2007**, *129,* 2369.
(3) Nafady, A. and Bond, A. M. *Inorg. Chem.* **2007**, 46, 4128.
(4) Nafady, A.; Bond, A. M.; Alexander Bilyk *J. Phys. Chem. C* **2008,** *112,* 6700.
(5) Nafady, A.; Bond, A. M. O'Mullane A. P. *Inorg. Chem.* **2009,** *48*, 9258.

STM Studies of Electrochemical Single Molecule Transistors

Richard J. Nichols*,† Nicola J. Kay,† Simon J. Higgins,*,† Jan O. Jeppesen,‡
Edmund Leary,†,⊥ Jess Lycoops,‡ and Jens Ulstrup,§
†Department of Chemistry, Donnan and Robert Robinson Laboratories,
University of Liverpool, Liverpool L69 7ZD, U.K.
‡Department of Physics, Chemistry, and Pharmacy, University of Southern
Denmark, Campusvej 55, DK-5230 Odense M, Denmark
§Department of Chemistry and NanoDTU, Technical University of Denmark,
DK2800 Kgs. Lyngby, Denmark
Nichols@liv.ac.uk

Measurement of the electrical properties of single molecules sandwiched between metal contacts has become an experimental reality over the last decade. In recent years, we have developed and exploited novel scanning-tunnelling-microscopy (STM) based methods for achieving this feat. This has included STM measurements of single molecule conductance under electrochemical potential control. The electrochemical potential can be used to control the redox state of single molecule bridges and switch the electrical conductance from low to higher values. This has been referred to as the “single molecule electrochemical transistor” configuration, with the electrochemical potential “gating” the molecular conductance in the STM nano-gap configuration. Recent results from our group on gating the conductance of single molecules will be discussed including studies of the redox active pyrrolo-tetrathiafulvalene (pTTF) molecular bridge. Using the STM in a room temperature ionic liquid environment enabled both the mono-cationic and the di-cationic redox states of the pTTF moiety to be studied in the molecular break junction configuration. As the electrochemical potential was swept through the 3 redox states of pTTF a clear “off−on−off−on− off” conductance switching behavior was observed. The mechanism of charge transport in the STM nano-gap setup is discussed as is the quantitative determination of reorganization energies and the comparison between ionic liquid and aqueous media. Our recent work on other redox active molecular wires studied using this in-situ electrochemical STM technique will also be discussed.

(1) Kay, N. J.; Higgins, S. J.; Jeppesen, J. O.; Leary, E.; Lycoops, J.; Ulstrup, J.; Nichols, R. J.: Single-Molecule Electrochemical Gating in Ionic Liquids. *Journal of the American Chemical Society* **2012**, *134*, 16817-16826.
(2) Sedghi, G.; Garcia-Suarez, V. M.; Esdaile, L. J.; Anderson, H. L.; Lambert, C. J.; Martin, S.; Bethell, D.; Higgins, S. J.; Elliott, M.; Bennett, N.; Macdonald, J. E.; Nichols, R. J.: Long-range electron tunnelling in oligo-porphyrin molecular wires. *Nature Nanotechnology* **2011**, *6*, 517-523.

In Situ Neutron Reflectometry Study of pH Effects on Hydrogen Absorption by Zirconium During Cathodic Polarization

J.J. Noël[1], J.M. Smith[2], Z.Tun[3], and D.W. Shoesmith[1,4]
[1] *University of Western Ontario, London, Ontario, Canada*
[2] *Atomic Energy of Canada Limited, Chalk River, Ontario, Canada*
[3] *Canadian Neutron Beam Centre, Chalk River, Ontario, Canada*
[4] *Surface Science Western, London, Ontario, Canada*
jjnoel@uwo.ca, smithjm@aecl.ca, zin.tun@nrc.gc.ca, dwshoesm@uwo.ca

Hydrogen (or deuterium), which can be produced as a by-product of corrosion reactions, is detrimental to the mechanical integrity of zirconium if absorbed into the metal, where it can form hydrides and lead to hydrogen-induced cracking. In this paper we describe the use of in situ neutron reflectometry to detect and quantify hydrogen and deuterium absorbed by zirconium metal during cathodic charging at different pH and applied potentials. The native air-formed oxide film on the zirconium surface, which is only a few nanometers thick, provides an excellent barrier to hydrogen entry into the underlying metal in neutral pH solution. The barrier quality of the oxide film was found to be strongly dependent on the pH of the solution in which it was polarized. Hydrogen absorption was not observed in neutral pH solution during cathodic polarizations as low as -2.5 V_{SCE}, however increasing amounts of hydrogen absorption readily occurred as the pH was lowered by addition of sulphuric acid to the solution.

Automated Patterning of Bare Metallic Nanostructures by Precisely Localized Electrorefining

Wojciech Nogala, Magdalena Kominiak, Kannan Palanisamy,
Sylwester Gawinkowski, Martin Jönsson-Niedziolka, Marcin Opallo
Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warsaw, Poland
wnogala@ichf.edu.pl

Research on more abundant non-platinum metal catalysts has attracted recently more attention because of development of alkaline direct ethanol fuel cells.[1] This trend is supported by the emergence of alkaline anion exchange membranes that conduct hydroxide ions.[2] Contrary to acidic environment (corrosive for non-noble metals), alkaline electrolyte allows to apply a wide range of metallic catalysts. The kinetics of both ethanol oxidation and oxygen reduction in alkaline media is faster than in acidic environment.[3,4] An additional advantage of ethanol is its uniquely high specific energy, non-toxicity and the fact that ethanol can be produced in large quantities from agricultural products or biomass.

Apart from electrocatalysis another popular application of metallic surfaces is Surface Enhanced Raman Spectroscopy (SERS). Gold, silver and copper nanoparticulate surfaces are known as good SERS supports.[5]

In this study micropatterned nanostructures of bare gold, silver and copper catalysts were obtained on tin-doped indium oxide (ITO) support by localized electrorefining using tip generation/sample collection mode of scanning electrochemical microscopy (SECM)[6]. Electrodeposition was carried out under control of inverted optical microscope. The influence of electrodeposition conditions on the morphology of obtained deposits was examined by scanning electron microscopy and atomic force microscopy. Relative electrocatalytic activities of various catalysts deposited on single ITO support towards reaction proceeded in alkaline fuel cells were determined by SECM. Maps of SERS spectra of preadsorbed porphycene selected as model system were recorded using Raman confocal microscopy.

References:

[1] E.H. Yu, X. Wang, U. Krewer, L. Li, K. Scott, Energy Environ. Sci. 5 (2012) 5668.
[2] H.Y. Hou, S.L. Wang, H. Liu, L.L. Sun, W. Jin, M.Y. Jing, L.H. Jiang, G.Q. Sun, Int. J. Hydrogen Energ. 36 (2011) 11955.
[3] A.V. Tripkovic, K.D. Popovic, B.N. Grgur, B. Blizanac, P.N. Ross, N.M. Markovic, Electrochim. Acta 47 (2002) 3707.
[4] J. Datta, A. Dutta, S. Mukherjee, J. Phys. Chem. C 115 (2011) 15324.
[5] P.L. Stiles, J.A. Dieringer, N.C. Shah, R.P. Van Duyne, Annu. Rev. Anal. Chem. 1 (2008) 601.
[6] R.G. Fedorov, D. Mandler, Phys. Chem. Chem. Phys. 15 (2013) 2725.

The unique binding properties of the flavoprotein dodecin studied with AFM force spectroscopy, QCM-D, and SPR

Gilbert Nöll,*[a] Björn Heidel[a], Sabine Wenderhold-Reeb[a], Holger Schönherr,[b] and Martin Grininger[c]
[a] *Siegen University, Fac. IV, Dept. Chem.-Biol., Organic Chemistry, Adolf-Reichwein-Str. 2, 57068 Siegen, Germany;* [b] *Siegen University, Fac. IV, Dept. Chem.-Biol., Physical Chemistry I, Adolf-Reichwein-Str. 2, 57068 Siegen, Germany;* [c] *Goethe University Frankfurt, Riedberg Campus FMLSBuilding, Max-von-Laue Str. 15, 60438 Frankfurt am Main, Germany.*
e-mail: noell@chemie.uni-siegen.de

Dodecin from *Halobacterium salinarum* is a dodecameric hollow spherical riboflavin binding protein. Dodecin (with a diameter of 6-7 nm) comprises six flavin binding pockets arranged at the angles of an octahedron. In each binding pocket up to two flavin ligands can be bound. In the binding pocket the flavins are arranged in an aromatic tetrade in between two tryptophans, which are part of the apoprotein. Dodecin binds oxidized flavins, whereas flavin reduction induces dissociation of the holoprotein in apododecin and free flavins. In order to study the apododecin-flavin binding interaction, different types of flavin-terminated DNA monolayers were prepared (dsDNA, as well as ssDNA were used), and the apododecin binding and unbinding kinetics depending on the flavin surface were studied by quartz crystal microbalance with dissipation mode (QCM-D), and surface plasmon resonance (SPR) measurements. Depending on the surface density of the adsorbed flavins, dodecin is captured by one or more flavins. For atomic force microscopy force spectroscopy (AFM-force spectroscopy), an AFM-tip was modified with flavin-terminated ssDNA, and the force, necessary for pulling the flavin out of the apododecin binding pocket, was measured. According to the results of the force spectroscopy measurements, the unbinding rate constant of a single apoprotein-ligand complex is $k_{off(AFM)} = 6.8 \cdot 10^{-3}\ s^{-1}$. QCM-D and SPR adsorption studies of the apododecin-flavin interaction revealed that, despite a relatively high off-rate constant, apoprotein-ligand binding can be considerably strengthened via multivalent interaction. It was found, that upon biospecific adsorption of apododecin on the surface modified with flavin-DNA ligands at high flavin surface density, the protein formed a stable monolayer and no significant desorption was observed during an extended period of time. Nevertheless, the apododecin flavin complex can easily be released by chemical flavin reduction. Binding and release of dodecin is a reversible process, which can be carried out several times with only minor aging of the surface (which might be a matter of optimization). Due to its unique binding properties, the apododecin-flavin complex holds great potential for applications in bio/nanotechnology similar to streptavidin-biotin.

Electrochemical Immobilization of Fibronectin on a Gold Surface: Control of Its Surface Conformation and Interaction with Endothelial Cells

S. Omanovic[1], M. Dargahi[1], V. Nelea[2], A. Mousa[2], M.T. Kaartinen[2,3]

1. Department of Chemical Engineering; 2. Faculty of Dentistry, 3. Faculty of Medicine, Division of Experimental Medicine, McGill University, Montreal, QC, Canada
sasha.omanovic@mcgill.ca

Coating medical implants with a high cell-functional extracellular matrix protein fibronectin (FN) by simple physical adsorption is a common technique employed to improve the biocompatibility of metal implants. However, FN needs to adopt a specific conformation on the implant surface in order to be active toward cell adhesion, and this proved to be difficult to control when FN is just physisorbed on the substrate surface. In addition, such an adsorbed protein molecule desorbs form the implant surface quickly, as the result of the blood shear stress.

This work presents results on the use of an electrochemically-based method to (*i*) irreversibly immobilize FN on a gold surface, (*ii*) control its conformation and (*iii*) the subsequent interaction of endothelial cells with the substrate surface. It was found that by controlling the surface charge externally, during the FN adsorption process, it is possible to control the surface conformation of the FN molecule; open-structure individual FN molecules and FN filaments were formed on a negatively charged substrate, while the FN conformation on a positively charged surface was globular and closed. Subsequent endothelial cell attachment results also showed that samples coated with FN in an open conformation could attract up to 60% more cells than a bare gold substrate, and 40% more cells than samples coated with FN in a closed conformation. This is due to the availability of FN cell-binding domains when FN adopts the open conformation on the surface. In addition, experiments in a stagnant buffer solution and a flow cell showed that FN immobilized on the gold and 316L stainless steel surface in an open conformation is very stable (irreversibly immobilized).

Effect of Nanotopography of Aluminum Surface and Crystal Orientation on Pore Initiation of Anodic Porous Alumina

Sachiko Ono and Hidetaka Asoh
Department of Applied Chemistry, Faculty of Engineering, Kogakuin University
2665-1 Nakano, Hachioji, Tokyo 192-0015, Japan
sachiono@cc.kogakuin.ac.jp

Anodic porous alumina, a typical self-ordered nanoporous material formed by the anodization of aluminum in an appropriate acidic solution, has recently been widely applied as a starting material for the fabrication of various types of nanodevice. To expand the application field of the ordered porous structure of anodic alumina, it is necessary to improve the regularity of pore arrangement and to clarify the mechanism of self-ordering behavior of anodic porous alumina. In addition, to elucidate the pore nucleation and growth of anodic porous alumina in the initial stage of anodization is also an important subject for both basic research and commercial applications. In particular, surface properties such as adhesion, hardness, tribology, adsorption of anodic films are primary dependent on surface pore morphology. In the present study, pore initiation and growth processes of anodic oxide films formed on differently pretreated aluminum substrates were investigated by atomic force microscopy, scanning electron microscopy and X-ray diffraction analysis with focusing on the crystal orientation and surface topography of aluminum substrate. Nanotopography of heated and subsequently electropolished aluminum surface was particularly affected by the crystal orientation of aluminum substrate, which is controlled by heating condition, as well as electropolishing voltage. In the initial stage of anodization, specific nanotopography of electropolished aluminum surface was served as the initiation sites for pore generation, and accordingly it influenced a porous cell arrangement. Using planarized aluminum with less than 0.3 nm asperities, however, a large number of fine pores initiated on the oxide film surface at the very first stage with the formation of porous cell protruded to the substrate. Thus, it was clarified that the growth of anodic oxide films was seriously influenced by the surface topography of aluminum substrate, which is dependent on the crystal orientation and pre-treatments.

Coupling of Faradaic and Charging Currents in Impedance Spectroscopy

Shao-Ling Wu,[1] Morgan Harding,[1] Mark E. Orazem,[1] Bernard Tribollet,[2] and Vincent Vivier[2]
[1]*Department of Chemical Engineering, University of Florida, Gainesville, FL USA*
[2]*LISE UPR15 du CNRS, Université Pierre et Marie Curie, Paris France*
meo@che.ufl.edu

While faradaic and charging currents are usually considered separately for simulations of impedance response,[1] Delahay[2] suggested in 1966 that the flux of reacting species should contribute to the charging of the interface as well as to the faradaic reaction. Recent simulations suggest that treatment of coupled faradaic and charging processes will give rise to CPE behavior.[3] This work made use of a mathematical structure for modeling coupled faradaic and charging processes that was described recently by Nisancioglu and Newman.[4]

Calculation of the impedance response associated with coupled charging and faradaic currents requires both a detailed microscopic model of the diffuse double layer and solution of coupled convective diffusion equations in the frequency domain. In the present work, a simplified model of the diffuse double layer is used to illustrate the influence on the impedance response of coupling and decoupling the charging and faradaic currents. The coupling of charging and faradaic currents is shown to yield a high-frequency dispersion, demonstrated here for deposition of silver in both poorly-supported and well-supported electrolytes. The frequency dispersion associated with coupled charging and faradaic currents may be explained in terms of an effective capacitance that accounts for the influence of concentration and that is shown to be a function of frequency.

The present work yields new insight into a commonly used experimental technique by coupling interfacial electrochemistry at the nanometer scale to frequency-domain continuum models.

References

1. J. H. Sluyters, *Recl. Trav. Chim. Pays-Bas*, **79** (1960), 1092-1100.
2. P. Delahay, *J. Phys. Chem.,* **70** (1966), 2373-2379.
3. S.-L. Wu, *Influence of Disk Electrode Geometry on Local and Global Impedance Response*, PhD Dissertation, University of Florida, Gainesville, Florida, 2010.
4. K. Nisancioglu and J. S. Newman, *J. Electrochem. Soc.,* **159** (2012), E59-E61.

Pd-Based Trimetallic Nanoparticles for Enhanced Hydrogen Storage

Cassandra Ostrom, Aicheng Chen
Department of Chemistry, Lakehead University
955 Oliver Road, Thunder Bay, Ontario P7B5E1, Canada
ckostrom@lakeheadu.ca, achen@lakeheadu.ca

Energy production and storage are crucial towards the development and sustainability of our current standards of living. Conventional methods of energy production (e.g. fossil fuels) impose negative environmental impacts, encouraging the development of green energy alternatives. Hydrogen fuel cells are promising solutions for the efficient and clean supply of electricity, but, require solving the issue of storage and transport of hydrogen. Recently, our group has focused on the hydrogen adsorption properties of carbon based materials modified with metallic dissociation catalysts [1-4]. In this presentation, we report on hydrogen electrosorption onto activated carbon materials modified with different trimetallic dissociation catalysts (Pd-Ag-Cd).

Pd-Ag-Cd nanoparticles were uniformly dispersed on the surface of activated carbon (Norit PAC200) using sodium borohydride reduction method. Using electrochemical methods, the optimized composition of the Pd-Ag-Cd alloys was determined to be $Pd_{80}Ag_{10}Cd_{10}$; with the highest hydrogen sorption capacity at a hydrogen desorption charge of 18.49 $C/cm^2 \cdot mg$. It was found that synergistic effects between the nanoparticles and carbon substrate drastically increased hydrogen storage capability. Our studies present Pd-Ag-Cd catalysts as attractive materials for use as hydrogen dissociation catalysts for applications in both hydrogen purification and storage.

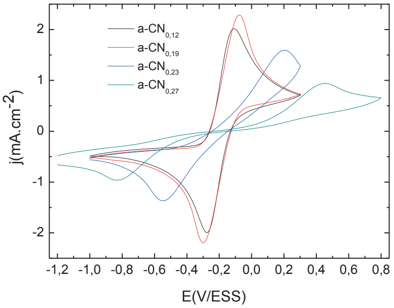
References:

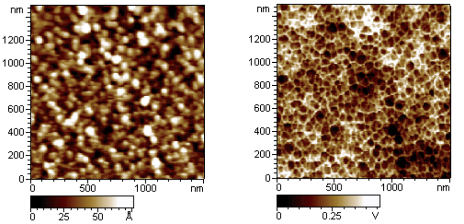
[1] B.D. Adams, C.K. Ostrom, S. Chen, A. Chen, High-performance Pd-based hydrogen spillover catalysts for hydrogen storage. J. Phys. Chem. C 114 (2010) 19875.
[2] S. Chen, B.D. Adams, A. Chen, Synthesis and electrochemical study of nanoporous Pd-Ag alloys for hydrogen sorption. Electrochim. Acta 56 (2010) 61.
[3] B.D. Adams, C.K. Ostrom, A. Chen, Hydrogen electrosorption into Pd-Cd nanostructures. Langmuir 26 (2010) 7632.
[4] C.K.Ostrom, A. Chen, Synthesis and electrochemical study of Pd-based trimetallic nanoparticles for enhanced hydrogen storage. J. Phys. Chem. C 117 (2013) 20456.

Amorphous carbon nitride thin films: versatile electrode materials with interdependent properties at the nanoscale

S. Jribi, M. Faure, F. Billon, C. Debiemme-Chouvy[1,2], C. Deslouis[1,2], J. Gamby, A. Pailleret[1,2]
[1]*CNRS, UPR 15 (LISE), 4, place Jussieu, case courrier 133, F-75005, Paris, France.*
[2]*UPMC Univ. Paris 06, UPR 15 (LISE), 4, place Jussieu, F-75005, Paris, France.*
e-mail address : alain.pailleret@upmc.fr

Amorphous carbon nitride thin films can be deposited on a large variety of substrates by using the reactive cathodic magnetron sputtering technique. The mutual reactivity existing between carbon and nitrogen in the plasma phase during the deposition step is known to lead to a large number of C/N functional groups in the bulk as well as on the surface of a-CN$_x$ materials. A brief overview of investigations related to this family of materials and reported recently in literature leads to the conclusion that various a-CN$_x$ materials can be produced whose surface properties depend mainly on the nitrogen content and also on various deposition parameters such as power, total pressure, use of RF applied on the substrate, or identity of the substrate for example.





AFM images (left: topography in the contact mode, right: surface conductivity in the current-sensing mode) obtained on a a-CN$_{0.36}$ thin film. Bias: 8 V.

Cyclic voltammograms obtained on a-CN$_x$ electrodes deposited on p-doped Si substrate without RF in a 10 mM Fe(CN)$_6^{3-/4-}$ aqueous solution containing also 0.5 M KNO$_3$. v = 50 mV/s. Ref : SSE. CE : Pt

Among interesting surface properties of these electrode materials, one can cite their smoothness (rms = 9 Å, see left AFM image), their inhomogeneous surface conductivity (see right surface conductivity image), their electrochemical activity (see CVs shown above), their surface functional groups among which amine groups were determined using the chemical grafting of a ferrocene redox probe and their subsequent electrochemical detection. The next challenge to be faced concerning a-CN$_x$ thin films is to optimize each of these surface properties predictably interdependent at the nanoscale with the help of adapted surface pre-treatments. Ongoing studies related to this objective will be introduced.

Structure of LiF on Graphene: The Role of Electrostatic Effects on Determining the Structure of Solid Electrolyte Interphase

Sara Panahian Jand, Payam Kaghazchi
Institute of Electrochemistry, Ulm University
Albert-Einstein-Allee 47, D-89069 Ulm, Germany
sara.panahian@uni-ulm.de

The solid electrolyte interphase (SEI) is a heterogeneous layer that is formed on the surface of anodes (e.g. graphene and graphite) in Li-ion batteries (LiB) during the first charging cycles [1]. Its formation is due to the reduction of electrolyte species on the anode surface. The SEI layer plays a key role in the safety and operating parameters of LiBs [2]. However, despite of its importance, only little is known about its atomistic structure and mechanism of its growing on the anode surface.

In this presentation, using DFT calculations and developing a simple electrostatic model we study the structure and growing mechanism of nanoclusters (NC) of lithium fluoride (LiF), which is a main component of the SEI layer, on graphene. We find that, independent of being in contact or not with the graphene surface, the LiF NCs with (100) facets are the most stable structures. These DFT results, which are in agreement with recent experimental observations showing formation of crystalline-LiF with (002) plane near the surface of graphene electrodes [3], can also be predicted by the simple electrostatic model for ionic NCs. In addition, we find that LiF(100)-NCs tend to grow in a 3-D mode, which can explain a recent experimental finding that show stabilization of sparsely distributed LiF nanoparticles with (002) plane on a synthesized LiF-modified graphene electrode (as a prelithiated electrode material) [4]. This work suggests that using a simple electrostatic model we can study the atomic structure and mechanism of growing of the SEI layer in LiBs [5].

[1] Jie Zhang et al., Nano Lett., **12** (4), 2153 (2012)
[2] Hui Wu, Nature Nanotechnology, **7**, 310 (2012)
[3] S. Chattopadhyay et al., Chem. Mater., **24**, 3038 (2012)
[4] Z-S Wu et al., Adv. Funct. Mater., **22**, 3290 (2012)
[5] S. Panahian Jand and P. Kaghazchi, Submitted

Electrodeposited Polymers From Triphenylamine-Based Hydrazones As Electronically Active Materials

Piotr Pander[1], Przemyslaw Data[1,2]
[1] *Silesian University of Technology, Faculty of Chemistry, Department of Physical Chemistry and Technology of Polymers, 44-100 Gliwice, Strzody 9, Poland;*
[2] *Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, Zabrze, Poland*
PanderPiotr@gmail.com

Recent interest in polymer optoelectronics and electronics leads to finding new electronically active materials for several applications. Aromatic hydrazones are very effective organic hole-transporting materials widely used e.g. in photoreceptors. Compounds 1 and 3 shown on Fig. 1 undergo thermal-initialized polymerization [1] however molecules 1-3 present the ability of obtaining polymer films by electropolymerization process. In this study we present results of electrochemical, spectrocelectrochemical and fluorescence investigation of polymers made by electropolymerization of monomers shown on Fig. 1. The polymers were synthesized on ITO coated glass (or quartz) electrodes from 0.1M Bu_4NBF_4 dichloromethane solution.

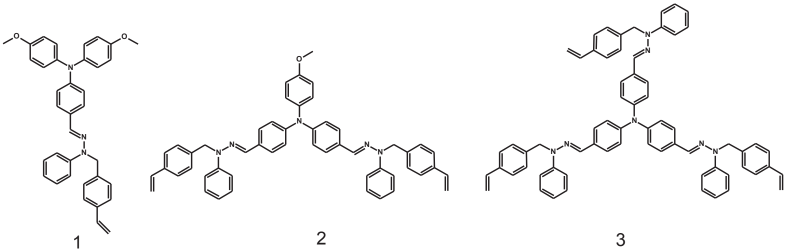


Fig. 1. Investigated compounds

Acknowledgement.
All monomers were synthesized by prof. Juozas Grazulevicius group from Kaunas University of Technology. This work was supported by Ministry of Science and Higher Education Project No. IP2012 039572.

References

1. V. Mimaite, J.V. Grazulevicius, J. Ostrauskaite, V. Jankauskas, *Dyes and Pigments*, **2012**, *9*, 47, 52

Limitations of Probing the Oxygen Reduction Reaction on the Millisecond Timescale due to Adsorbed Oxygen

Samuel Perry, Guy Denuault
University of Southampton
School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK
scp2g08@soton.ac.uk

The oxygen reduction reaction (ORR) may proceed via either a two electron pathway, through a peroxide intermediate, or a four electron direct reduction. If the rate of mass transport is high, the rate of diffusion away from the electrode increases, and so the apparent number of electrons transferred (n_{app}) ends up being less than four. In the steady state, n_{app} has been previously determined by rotating disc electrode, microelectrodes [1] and scanning electrochemical microscopy [2]. However, to our knowledge, it has not been reported how n_{app} depends on the timescale of observations.

The number of electrons transferred during reduction was probed using sampled current voltammetry (SCV). This is a multistep procedure that builds a current transient by recording the current separately for each potential along the reduction wave using a series of potential step experiments. This allows the current to be recorded from the same starting point at each potential, and for the electrode to be pre-treated between each data run using the same conditioning waveform.

Sampling the current at the same time after the potential step on each transient allows as SCV to be constructed. In this way, multiple SCVs can be recorded from the same collection of transients. The current was normalized by dividing the experimental current by the theoretical diffusion controlled current reported by Mahon and Oldham[3] for a one electron process. This causes the data to converge to n_{app}. The method was verified using the single electron reduction of ruthenium hexamine as a model system, before being used to probe the transient oxygen reduction.

It was found that short time measurements of the ORR gave an unexpectedly large current under certain conditions, but not under others. By varying the electrode material, electrolyte, pH and collection waveform, the role of surface adsorbed oxygen prior to the potential step in causing this extra current was probed. This presentation will look at evidence supporting adsorbed oxygen as the cause of extra current, which therefore questions the validity of transient measurements for ORR.

[1] D. Pletcher, S. Sotiropoulos, *J. Electroanal. Chem.* **1993**, *356*, 109-119.
[2] A. J. Bard et al, *Anal. Chem.* **2008**, *80*, 3254-3260.
[3] P. J. Mahon, K. B. Oldham, *Anal. Chem.* **2005**, *77*, 6100-6101.

The Effects of Conducting Polymers on Formic Acid Oxidation at Pt Nanoparticles

Peter G. Pickup, Reza B. Moghaddam
Memorial University
Department of Chemistry, St. John's. NL A1B 3X7, Canada
ppickup@mun.ca

Although it is well known that the incorporation of conducting polymers into fuel cell catalysts can enhance their activities, our understanding of the origins of these effects is very rudimentary. In part, this is due to the very diverse range of materials and synthesis methods that have been employed, and difficulties in fully characterizing these systems. We have therefore adopted simple methodology for systematic investigation of these effects in which a thin layer of the polymer, on a glassy carbon substrate, is coated with approximately a monolayer of preformed and well characterized Pt nanoparticles [1]. The effects of polyaniline, polypyrrole, polyindole and polycarbazole on formic acid oxidation will be compared.

Mechanistic insights have been obtained by comparing the effects of the above polymers with their monomers in solution [2]. In addition, CO stripping and voltammetric oxidation of poisons has been employed in the case of polycarbazole [3]. The wide range of different polymers that exhibit beneficial effects, similar effects seen with some monomers, and the effects of polycarbazole on CO oxidation all suggest that the interaction of the polymer/monomer π-system with the Pt nanoparticles may cause an electronic effect on formic acid oxidation. Changes in binding energies from X-ray photoelectron spectroscopy support this hypothesis.

References

1. R.B. Moghaddam and P.G. Pickup, Oxidation of formic acid at polycarbazole-supported Pt nanoparticles, Electrochimica Acta 97 (2013) 326.
2. R.B. Moghaddam and P.G. Pickup, Influences of aniline, carbazole, indole, and pyrrole monomers and polymers on formic acid oxidation at Pt electrodes, Electrochimica Acta 107 (2013) 225.
3. R.B. Moghaddam and P.G. Pickup, Mechanistic studies of formic acid oxidation at polycarbazole supported Pt nanoparticles. Electrochim. Acta 111 (2013) 823.

In situ STM studies of Cd(0001) electrode in aqueous electrolyte solution

Piret Pikma, Vitali Grozovski, Enn Lust
Institute of Chemistry, University of Tartu
Ravila 14a, Tartu 50411 Estonia
piret.pikma@ut.ee

The main aim of this study was to develop the experimental conditions needed to obtain the atomic resolution STM data within the ideal polarization region of the Cd (0001) electrode [1].

The in situ STM studies of Cd(0001) single crystal electrode, which was electrochemically polished [2], have been performed under negative polarisations from -0.92 to -1.5 V (versus Ag|AgCl in saturated KCl aqueous solution) in 0.1 M $Na_2SO_4 + 10^{-5}M\ H_2SO_4$ aqueous solution.

The in situ STM data show that the surface structure of the Cd(0001) consists of atomically flat terraces (Fig. 1 (a)) and is stable within the potential region investigated. According to the data in Fig. 1(b,c) the regular atomic structure can be observed with interatomic distances d = 2.9±0.1 Å, which are in a good agreement with Cd(0001) crystallographic parameters applying hexagonal close-packed structure model for Cd(0001) plane.

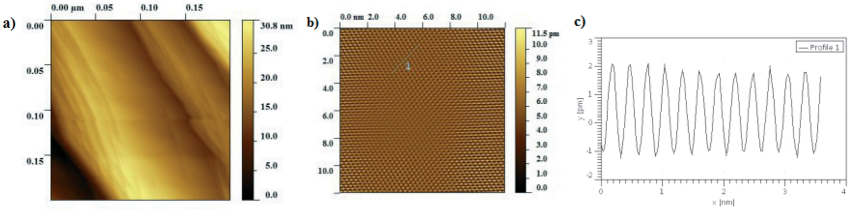


Fig.1. In situ STM image (a), atomic resolution image (b) and compatible height profile (c) for Cd(0001) electrode in 0.1 M $Na_2SO_4 + 10^{-5}M\ H_2SO_4$ aqueous solution at E = −1.15 V.

Acknowledgements: The present study was supported by the Estonian Center of Excellence: High technology materials for sustainable development, by the Estonian Ministry of Education and Research project SF0180002s08 and by graduate school „Functional materials and processes" (European Social Fund, project 1.2.0401.09-0079).

References:

1. L. Siinor, V. Ivaništšev, K. Lust and E. Lust, J. Solid State Electrochem. 14 (2010) 555
2. E. Lust, A. Jänes, K. Lust, V. Sammelselg, P. Miidla, Electrochim. Acta 42 (1997) 2861

Quantitative SNIFTIRS study of the adsorption of adenine on Au(111) electrodes

Francisco Prieto[a), Zhang Fei Su[b), John Jay Leitch[b), Jacek Lipkowski[b) and
Manuela Rueda[a)
[a)Department of Physical Chemistry University of Seville.
c/ Profesor Garcia Gonzalez 2. 41012 Seville. SPAIN
[b) Electrochemistry Technology Centre. Department of Chemistry.
College of Physical & Engineering Science. University of Guelph
Guelph, Ontario, CANADA. N1G 2W1
dapena@us.es

The adsorption of DNA bases on electrode-solution interfaces is an interesting subject because of the biological relevance of these molecules and the fact that most of the processes taking place at biological interfaces involve electrochemical phenomena.

In previous work, the adsorption of adenine on Au(111) electrodes has been studied by means of a combination of electrochemical, spectroscopic and microscopic techniques [1]. These studies have concluded that adenine is partially tilted relative to the elecrode, and that the coordination to the metal takes place trough the amine group nitrogen (N_{10}) and trough another nitrogen, either the pyrimidine ring nitrogen N_1 or the imidazol ring nitrogen N_7.

Quantitative SNIFTITRS has proved to be a powerful tool to obtain quantitative information about the orientation of small soluble molecules adsorbed on an electrode surface [2]. This method allows one to measure the angle between the direction of the transition dipole moment of a given vibration in adsorbed molecule and the direction normal to the electrode. Here we describe studies of the adsorption of adenine on the Au(111) electrode by means of the quantitative SNIFTIRS method in order to get the quantitative information about the orientation of this molecule on the electrode surface and its dependence on the applied potential.

1.- A. Rodes, M. Rueda, F. Prieto, C. Prado, J.M. Feliu, A. Aldaz, J. Phys. Chem. C 113 (2009) 18784.

2.- V. Zamlynny, J. Lipkowski in Advances in *Electrochemical Science and Engineering: Diffraction and Spectroscopic Methods in Electrochemistry*, Vol 9, R.C. Alkire, D.M. Kolb, J. Lipkowski, P. N. Ross eds., 2006 WILEY-VCH. (and references there in).

A new model of non-equilibrium electrochemical interfaces in electrochemical energy conversion

Matias A. Quiroga*[1,2], Kan-Hao Xue[1,2], Trong-Khoa Nguyen[1,2], He Huang[1,2],
Michal Tulodziecki[1,2], Alejandro A. Franco**[1,2]

[1] *Laboratoire de Réactivité et de Chimie des Solides (LRCS), Université de Picardie Jules Verne & CNRS, UMR 7314 – 33 rue St. Leu, 80039 Amiens, France*

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

* *matqui@u-picardie.fr* ** *alejandro.franco@u-picardie.fr*

The nanometric liquid/solid electrochemical interface is the pivotal scale behind the operation of fuel cell and battery electrodes, and developing a deep understanding of its functional role is crucial to help enhancing the performance and the durability of these zero-emission devices [1-3].

We present here a new Mean Field theory describing electrochemical double layers (EDL) under non-equilibrium conditions at the vicinity of active electrode surfaces, thus in conditions where REDOX reactions occur. The theory explicitly accounts for finite ion size effects, solvent polarization effects and self-structuration of charged polymers in the electrolyte, and competitive adsorption/desorption and electrochemical reactions on the electrode surface [4]. The theory is "universal" as it can be used for the simulation of any kind of electrode/liquid electrolyte interface, for any ionic concentration: diluted concentration models (Poisson-Nernst-Planck) and ionic liquids are particular cases captured by the theory.

The application of this theory is illustrated through the simulation of the Oxygen Reduction Reaction on Pt(111) with an electrolyte constituted of water and a proton conducting PerFluoroSulfonic Acid (PFSA) polymer, an electrochemical interface representative of Polymer Electrolyte Fuel Cell electrodes. The theory is solved by coupling a Mean-Field ionic transport model with a LRCS house-made Kinetic Monte Carlo (KMC) package (*Monte Carlo Electrochemical Software for Surfaces Innovation*, "MESSI") which implements a Variable Step Size Method, parameterized with activation energies calculated from Density Functional Theory. Several simulations have been performed in different situations (applied constant and dynamic charge densities at the Pt surface, Pt surface with defects, different polymer/water volume fractions) in order to understand the impact of the EDL structural evolution onto the electrochemical observables (cyclic voltammetry and polarization curves) in comparison with experimental data [5].

[1] A.A. Franco, K. H. Xue, *ECS J. Solid State Sc. Tech.*, **2** (10) (2013) M3084.
[2] A.A. Franco, *RSC Advances*, **3** (32) (2013) 13027.
[3] A.A. Franco *et al.*, *Electrochim. Acta*, **56** (28) (2011) 10842.

On the Properties of Anodic Oxide Films of Nanostructured Zn and Zn Alloy Coatings

R. Ramanauskas, L. Gudavičiūte, A. Kosenko, O. Girčienė
Centre for Physical Sciences and Technology, Institute of Chemistry
Goštauto 9, LT-01108, Vilnius, Lithuania
ramanr@ktl.mii.lt

Oxide film formation on the surfaces of Zn and Zn-Ni (12%) coatings was studied with the aim to determine the influence of the electrode nature, grain size and film formation condition on the composition, thickness, protective and semiconductor properties of the oxide layers. Non-stationary (pulse) electrodeposition was applied as a means of metal structure modification. Voltammetric and EIS measurements in alkaline solutions were carried out for the oxide film thickness and semiconductor properties evaluation, respectively. XRD measurements yielded information on the texture, grain size, lattice imperfection and phase composition, while, AFM and SEM studies were applied for surface topography examination and XPS was used for the oxide film composition studies.

Oxide films formed on the both substrates consisted of $Zn(OH)_2$ and ZnO phases. Oxidized Zn-Ni surface exhibited higher protective abilities and possessed a higher amount of ZnO (~65 % of oxide layer was composed of ZnO), while the film on the Zn surface was less protective and contained only 44% of ZnO. The latter fact sustains the idea that films possessing higher amounts of ZnO are more resistant.

Similar investigations were carried out with the pulse plated Zn and Zn-Ni samples, which possessed different grain size, however, the same texture, phase and chemical composition. The grain size of investigated electrodes varied between 90 and 40 nm and did not caused any significant changes in the composition and porosity of the oxide films formed. The increase in the grain size of Zn electrode was accompanied by the decrease in the number of the metal lattice imperfections, what have caused the increase in the thickness of the oxide layer formed and the reduction of both, the values of polarization resistance (Rp) and donor concentration. The increment in the grain size of Zn-Ni substrate did not effected the Rp values of oxidized electrode, meanwhile, the oxide layer thickness and donor concentration values showed a tendency to reduce with the increase in the grain size of Zn-Ni coating.

The differences in the corrosion behavior of Zn and its alloy coatings can be explained by the obtained parameters of the oxide layers formed on their surfaces

In situ Raman Spectroscopy for Electrochemical Interfaces

Bin Ren, Zhi-Cong Zeng, Jin-Hui Zhong, Xiaobing Lian, Sheng-Chao Huang,
Mao-Hua Li, Teng-Xiang Huang
State Key Laboratory of Physical Chemistry of Solid Surfaces, MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, Collaborative Innovation Center of Chemistry for Energy Materials, Xiamen University, Xiamen 361005, China
bren@xmu.edu.cn

The interfacial structure and property of an electrochemical system is vitally important to the performance of electrochemical devices.

Non-traditional methods are attracting increasing interest due to their capability to provide the molecular level information. Among them, Raman spectroscopy is of particular interest. It can provide fingerprint information of electrochemical interfaces without bothering the water or CO_2 contents. Therefore, it has been widely used in electrochemistry.

We aim at developing electrochemical Raman methods that allows us to sensitively monitoring the electrochemical systems from the following points:

1. To obtain the bulk electrode material during the electrochemical reaction processes (such as the charging and discharging processes in the lithium ion batterier). It allows us to extract the detailed structure change of the electrode materials during the cycling process.
2. To reveal the interfacial properties of single layer graphene, including the capacitance, potential of zero charge and role of defects on the electrochemical activity of graphene.
3. To reveal the reaction and adsorption configuration of small molecules by using surface-enhanced Raman spectroscopy. For this purpose, we developed sophisticated in situ Raman cell to allow the study to be carried under the potential and temperature and solution flow control.
4. To develop electrochemical tip-enhanced Raman spectroscopy that allows us to study the electrochemical process on atomic smooth single crystal surface without any surface enhancement effect from the metal nanoparticles. Equally important is to develop reliable TERS tips that can be used under electrochemical conditions.

The future plan is to develop Raman-based imaging technique to dynamically following the electrochemical process with spatial information

Acknowledgement: This project was supported by NSFC (21021120456, 21021002 and 21227004) and MOST (2011YQ03012406) .

Oral presentation

Electrochemisty of Electroactive Ionic Liquids Modified with Ferrocene Redox Centers

Dominic Rochefort, Bruno Gélinas, Han Jin Xie, John Forgie
Département de chimie, Université de Montréal
C.P.6128 Succ. Centre-Ville, Montréal, Qc H3C 3J7
dominic.rochefort@umontreal.ca

Research on ionic liquids (IL) is motivated in large part by the almost endless possibilities of chemical modifications that can be made to one of their components to impart a specific functionality to the melt. A neat example of functionalized ionic liquid is found through the modification of alkylimidazoliums with a ferrocenyl redox moiety, resulting in an intrinsically electroactive liquid. Work on redox active polyether hybrid molten salts and other related systems demonstrated that the investigation of such redox ionic liquids phases can lead to new knowledge on electron transfer in liquid phases due to the intimate proximity of redox centers that cannot be achieved in solute-solvent systems. This contribution describes the properties of new electroactive ionic liquids which are obtained by the modification of either the alkylimidazolium cation or the bis(trifluoromethane)sulfonamide anion (Fig. 1). The electrochemical behavior of such redox ionic liquid phases was studied with the aim of understanding the interaction taking place between the anion and the cation. In particular, the redox ionic liquid obtained by the anion modification with ferrocene (ferrocenylsulfonyl-(trifluoromethylsulfonyl)imide, FcTFSI) showed an unusual behavior at high concentrations and in the absence of supporting electrolyte. The formation of a zwitterion upon oxidation of the anionic ferrocene-modified TFSI generates a diffusion layer with different properties from those of the bulk, decreasing mass transport of species at the electrode.

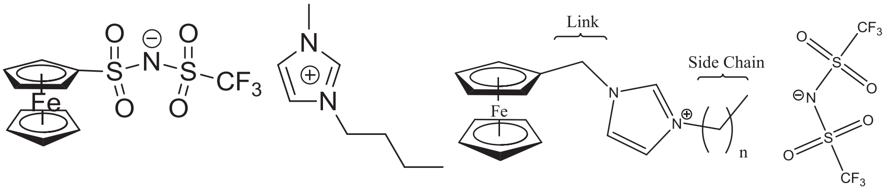


Fig. 1. Ionic liquid ions modified with ferrocene.

The effect of the type of ionic liquid, the nature of the substituent and on the alkyl chain length on the electrochemical and physico-chemical properties of the ionic liquids will be discussed with the aim of understanding the role of these parameters in the transport and electron transfer properties in redox ionic liquids.

Nanoscale Electrochemical Characterization of Materials by Means of Spatially Resolved Electrostatic Force, Current and Strain Measurements

M. Gellert[1], J. Siebert-Krümpelmann[1], V. Lushta[2], D. Ebeling[2],
A. Schirmeisen[2], B. Roling[1]
[1]Department of Chemistry, University of Marburg
Hans-Meerwein-Straße, 35032 Marburg/Germany
[2]Institute of Applied Physics, University of Giessen,
Heinrich-Buff-Ring 16, 35392 Giessen/Germany
roling@staff.uni-marburg.de

The usage of a conductive AFM tip as working electrode allows for a nanoscale electrochemical characterization of materials and interfacial processes. After applying a tip bias, electrostatic forces [1], currents [2] and strains [3] can be measured with a spatial resolution determined by the tip diameter. We discuss the performance and limits of such measurements for studying local ion transport and local electrochemical processes. In particular, measurements of electrostatic forces and electrochemically induced strains using cantilever resonance methods exhibit a very high sensitivity.

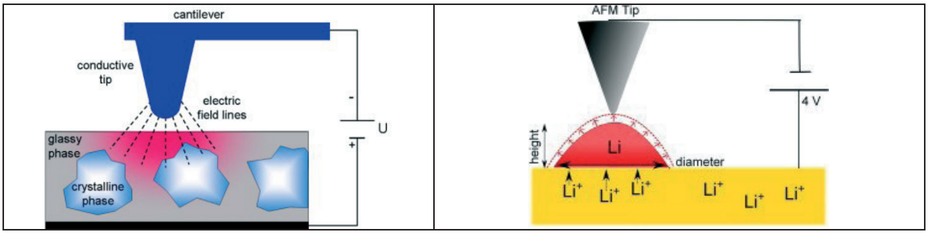


Figure 1: a) Setup for electrostatic force spectroscopy on a heterogeneous ion conductor; b) Setup for local lithium particle formation on a lithium ion conductor.

[1] A. Schirmeisen, B. Roling in 'Scanning Probe Microscopy for Energy Research' World Scientific Publishing Co. Pte. Ltd., Singapore, 2013.
[2]] J. Krümpelmann, H. Reinhardt, C. Yada, F. Rosciano, N. Hampp, B. Roling, *Solid State Ionics* **234** (2013) 46-50.
[3] S. Jesse, N. Balke, E. Eliseev, A. Tselev, N. J. Dudney, A. N. Morozovska, S. V. Kalinin, *ACS Nano* **5** (2011) 9682.

FT-IR Spectroelectrochemical Study of Adenine and Thymine Adsorptions and co-Adsorption on Gold Electrodes: The influence of pH.

Manuela Rueda[a)], Francisco Prieto[a)], Julia Alvarez-Malmagro[a)], Antonio Rodes[b)]
[a)]Department of Physical Chemistry University of Seville.
c/ Profesor Garcia Gonzalez 2. 41012 Seville. SPAIN
[b)] Department of Physical Chemistry and Institute of Electrochemistry.
University of Alicante. Ap. 99, E-03080, Alicante (Spain).
e-mail: marueda@us.es

Adenine and thymine are complementary DNA bases that play important roles in genetic expression and replication and in some enzymatic processes. Therefore, it can be interesting to study the adsorption of these molecules on electrodes by modern in-situ FT-IR methodology, that can provide detailed microscopic information about the orientations and interactions of the adsorbed molecules.

Previous studies have shown that both adenine and thymine get adsorbed on gold electrodes [1-2]. The study of the influence of pH can be interesting because it is known that the proportion of the different tautomeric forms of DNA bases can change with pH and it is well established that the presence of "unstable" tautomeric forms can induce unpaired bases interactions which seem to be related to some illness.

Recently, we have studied the co-adsorption of adenine and thymine on gold electrodes in acid solutions by ATR-SEIRAS experiments and found that both molecules rearranged on the electrode surface in a cooperative process in order to facilitate the Watson–Crick (W–C) and/or Hoogsteen (HG) interactions between the bases [3].

In this communication a comprehensive study is presented of the adsorption of adenine and of thymine and the co-adsorption of both bases in the pH range from 1 to 11. The experiments have been performed using H_2O and D_2O as solvents. The SNIFTIRS methodology is applied for the experiments with Au(111) electrodes and the ATR-SEIRAS for the experiments with thin-film gold electrodes.

The results are explained in terms of the adsorption of the three forms of adenine which are related by two acid-base equilibriums (pKa values in solution 4.2 and 9.8), the two thymine forms related by one acid-base equilibrium (pKa value in solution 9.5) and their respective enol-imino tautomeric forms.

1.- A. Rodes, M. Rueda, F. Prieto, C. Prado, J.M. Feliu, A. Aldaz, J. Phys. Chem. C 113 (2009) 18784; M. Rueda, F. Prieto, A. Rodes, J.M. Delgado, Electrochim. Acta, 82 (2012) 534.

2.- B. Roelfs, E. Bunge, C. Schröter, T. Solomun, H.Meyer, R.J. Nichols, H. Baumgärtel, J. Phys.Chem. B 101 (1997) 754; W. Haiss, B. Roelfs, S.N. Port, E. Bunge, H. Baumgärtel, R.J. Nichols, J. Electroanal. Chem. 454 (1998) 107.

3.- M. Rueda, F. Prieto, J. Alvarez-Malmagro, A. Rodes Electrochem. Comm. 35 (2013) 53

Potential-Driven Dynamics of Ultra-Thin Liquid Films on Au(111) Electrode

Takamasa Sagara, Ken Ozera, Shoma Murakawa, Hironobu Tahara
Division of Chemistry and Materials Science, Graduate School of Engineering
Nagasaki University, Bunkyo 1-14, Nagasaki 852-8521m Japan
e-mail: sagara@nagasaki-u.ac.jp

Gabriel Lippmann published in 1875 an outstanding paper on electrowetting with an address on electromechanical actuation [1]. Potential difference between an electrode immersed in a droplet of aqueous electrolyte solution placed on a thin insulator film and an underlying electrode can force active motions of the droplet. On the other hand, Ivošević and Žutić demonstrated spreading and detachment of insulating hexadecane droplets (2.5 mm size) on a Hg electrode surface in aqueous electrolyte solution [2]. Although unknowns still remains in electrochemical control of the droplet motions in both systems, insoluble liquid thin films or droplet arrays should join an important class of functional electrode surface modifiers. In sharp contrast to steady and robust SAM platforms, dynamic deformability of ultra-thin liquid films may find its use in many applications even in state-of-the-art fabrication of molecular electronic devices [3]. Droplet reshaping is brought about by surface tension balance, density differences, fluctuations, and hydrodynamic factors. Achievement of electrochemical fine control over the sharp and quick motion of a droplet and its spreading with high reversibility, large amplitude, and long term stability should be our research target.

We describe potential-driven dynamics of ultra-thin liquid films of long-chain molecules, such as hexadecane and 1-chlorohexadecane, on a Au(111) electrode surface. One of the well-suited methods to track the potential dependent droplet formation is *in situ* fluorescence microscopy [4]. Quenching of fluorescence from photo-excited probe molecules in the proximity (~25 nm) of the metal surface can be a measure of surface-normal distance. We newly obtained a set of distance scale fluorescence data, which was then tested for potential dependent assembling structural changes of amphiphilic molecular films of a few monolayer thickness.

References:

[1] G. Lippmann, *Ann. Chim. Phys.*, **5**, 494 (1875) [Translation into Engl. in *J. Phys.: Condens. Matter*, **17**, R705 (2005)]. [2] N. Ivošević, V. Žutić, *Langmuir*, **14**, 231 (1998). [3] T. Sagara, in *Bottom-up Nanofabrication: Supramolecules, Self-Assemblies, and Organized Films*, Vol. 3, Eds. K. Ariga, H. S. Nalwa, American Scientific Publishers, Valencia, Chap. 13, 347 (2009). [4] D. Bizzotto J. L. Shepherd, in *Advances in Electrochemical Science and Engineering: Diffraction and Spectroscopic Methods in Electrochemistry*, Vol. 9, Eds. R. C. Alkire, D. M. Kolb, J. Lipkowski, P. N. Ross, Wiley-VCH, Weinheim, Chap. 3, 97 (2006).

Improved carbon-carbon bond splitting using Pd catalysts grown by Atomic Layer Deposition onto TiO_2 nanotubes

L. Santinacci[1], L. Assaud[1], N. Brazeau[2], K. Pitzschel[1], V. Heresanu[1],
M. Hanbücken[1] and E. A. Baranova[2]
[1] CINaM-CNRS, Aix-Marseille University, Campus de Luminy, Marseille, France
[2] Dept Chemical and Biological Engineering, Centre for Catalysis Research & Innovation, University of Ottawa, Ottawa, Canada

Due to their low environmental impact and high power generation, fuel cells are promising alternative in automobile industry. The manufacturing of direct oxidation fuel cells by degradation of organic molecules, such as ethanol or methanol, using electrocatalysis is an attractive way to produce green energy. Direct Ethanol Fuel Cells (DEFCs) offer significant advantages due to ethanol non-toxicity and renewability and its high power density. Development of efficient catalysts for ethanol oxidation that break C–C bond and produce CO_2 has attracted great attention and represents one of the major challenges in electrocatalysis. The use of metal oxides such as CeO_2, SnO_2 and TiO_2 are interesting alternative to the usual C-based supports because they exhibit a longer stability.

In the present work, atomic layer deposition (ALD) has been used to deposit Pd nanoparticles onto TiO_2 nanotubes (TiO_2-nt) grown by aqueous anodic oxidation. The Pd deposition parameters have been investigated by scanning electron microscopy, transmission electron microscopy (Fig. 1), x-ray diffraction and x-ray photoelectron spectroscopy. It demonstrates that ALD is a powerful tool to functionalize such three-dimensional nanostructures. The electrocatalytic performances of the Pd/nt-TiO_2 systems for the ethanol electrooxidation has been tested in 1 M KOH + 1 M C_2H_5OH by cyclic voltammetry and chronoamperometry. A high electrocatalytic activity has been measured and, as expected, the electrochemical response evolves with the Pd loading. Additionally, it has been observed that the crystalline structure of the nt-TiO_2 has also a strong influence on the ethanol electrooxidation. Since promising results have been obtained with Pd/nt-TiO_2 systems, preliminary experiments have been performed by depositing the Pd clusters onto nt-TiO_2 covered by an ALD SnO_2 coating. A comparison of the electrochemical performances will be presented.

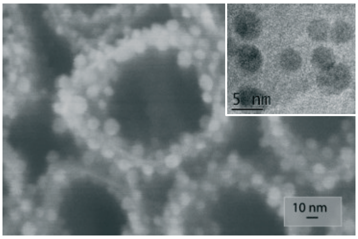


Fig. 1: SEM top view of nt-TiO_2 with Pd deposit. Inset: TEM view of the Pd catalysts.

Graded and Homogeneous CGO/LSCF cathode for IT-SOFC

Jaroslaw Sar[1,2], Laurent Dessemond[1], Elisabeth Djurado[1], Amélia Almeida[2]
[1]LEPMI, UMR 5279 CNRS, Grenoble University
1130 Rue de la Piscine, 38402 St. Martin d'Hères, France
[2]Dep. Eng. Quimica, IST-Technical University of Lisbon
1 Av. Rovisco Pais, 1049-001 Lisbon, Portugal
Jaroslaw.Sar@lepmi.grenoble-inp.fr

The role of Solid Oxide Fuel Cells (SOFC) is to produce electrical energy based on electrochemical reactions between fuel and oxygen operating at around 1000°C. The main research in this domain is to decrease working temperature below 700°C (IT-SOFC) to increase durability and reduce overall costs.

The aim of this work is to describe the electrochemical properties of innovative nanostructured $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) / $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) composite introducing a thin dense CGO layer between the porous CGO/LSCF cathode and YSZ electrolyte. CGO/LSCF cathode with graded and homogeneous composition was coated by Electrostatic Spray Deposition (ESD) on YSZ substrate [1]. The as-deposited coatings present highly porous microstructure referred to as coral with nano- and micro-scale porosity as observed by SEM-FEG. A second layer of LSCF was screen-printed at the top of coral microstructure to ensure a good current collecting. Electrochemical impedance spectroscopy was performed at Open Circuit Potential (OCP) during thermal cycles between 400°C and 700°C in static air. The ageing behavior of investigated assemblies was studied during isothermal dwells at 600°C for 200h in static air. No significant increase of both series resistance and electrode area specific resistance (ASR) after 200h at 600°C was recorded, evidencing the chemical stability of investigated electrodes. The ASR was found to decrease by a factor of 1.5 when a LSCF current collector layer (CCL) was applied with comparison to samples with no CCL.

To conclude, the gradient in CGO/LSCF composition has not a beneficial influence on electrical performances of CGO/LSCF cathode.

[1] Sar J., Charlot F., Almeida A., Dessemond L., Djurado E., Fuel Cells – from Fundamentals to Systems, to be published (2013)

Modeling Dye Sensitized Solar Cells Based on Nano Tubes or Nano Rods - A New Transmission Line Approach

P. Schmuki [a], C. Böhmer [b], F. Richter [b], C.A. Schiller [b,*]
[a] *Department of Materials Science and Engineering, WW4-LKO, University of Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany*
[b] *ZAHNER-elektrik, Thüringer Str. 12, 96317 Kronach, Germany*
[*] *Corresponding author: cas@zahner.de, phone +49926196211924*

In dye sensitized solar cells, DSSC, the electrons generated by photon absorption through the dye molecules appears in the bulk of the semi-conducting oxide material and mostly not in direct vicinity to the current collecting photo-anode. The efficiency of a DSSC may therefore suffer from the competition between charge transport- and loss processes. Intensity modulated photo spectroscopy of current, IMPS, and voltage, IMVS, are popular techniques for their investigation and the results are usually interpreted in terms of trapped electron diffusion- and recombination time constants [1].

The idea behind ignores the porous nature of the oxide material, what motivated some authors for the development of more appropriate alternative models. L. Bay and K. West [2] proposed a transmission line model, TLM, approach assuming a charge transport- and loss distributed over the grains of the porous oxide. This way, DSSC built from nano-porous oxide materials can be successfully modelled, but the dynamics of DSSC built from highly ordered TiO_2-nano-tubes or ZnO-nano-rods cannot be simulated with the same accuracy. The reason is that the TLM model after L. Bay and K. West does not take into account the contributions of the dedicated areas on the pore ground and at the tube / rod end (electrolyte side) to the overall response.

The authors will present an analytical model, which can be understood as photo-electrical equivalence to the very complete Homogeneous Pores Model after H. Göhr [3]. In the corresponding TLM terminating elements consider the contribution of the pore ground and the top area to the impedance as well as to the photoelectric transfer functions IMPS and IMVS.

The model was used for the efficiency analysis of complete thin film DSSC built from TiO_2-nano-tubes grown on Ti-metal [4]. The results will be presented.

[1] J. Bisquert, V.S. Vikhrenko, *Interpretations of the Time Constants Measured by Kinetic Techniques in Nanostructured Semiconductor Electrodes and Dye-Sensitized Solar Cells*, J. Phys. Chem. B 108 (2004) 2313-2322.

[2] L. Bay, K. West, *An equivalent circuit approach to the modelling of the dynamics of dye sensitized solar cells*, Solar Energy materials and Solar Cells, 87 (2005) 613.

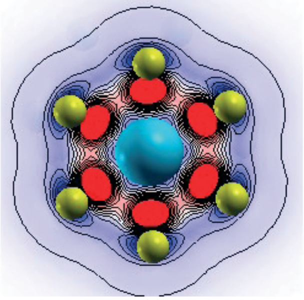
[3] H. Göhr, *Impedance Modelling of Porous Electrodes*, Electrochemical Applications, ZAHNER-elektrik, 1, 7-9 (1997), www.zahner.de/downloads/ea1997.pdf.

Double-layer properties of several modifications of carbon – a theoretical study

Wolfgang Schmickler, Noelia Luque, Paola Quaino, Fernanda Juarez, Leila Mohammadzade
Institute of Theoretical Chemistry, Ulm University
D-8073 Ulm
Wolfgang.Schmickler@uni-ulm.de

Carbon is a very versatile electrode material and exists in various forms, from graphite to graphene, nanotubes, and diamond. We have investigated the double-layer properties of several modifications of interest to electrochemistry. Graphite, which is the most common electrode carbon electrode, has an indirect band gap and a low density of states at the Fermi level. As a consequence, an external electric field can penetrate over a distance of several Ångstroms into the surface. Consequently, the double-layer capacity of a graphite electrode in contact with an aqueous solution is small, and it has a pronounced minimum at the potential of zero charge. Our model calculations, performed for high electrolyte concentrations, agree quantitatively with experimental data.

Doping carbon with nitrogen significantly changes its electronic properties. In particular, it enhances the density of states near the Fermi-level, which entails a better screening of external fields and an increase of the interfacial capacity. However, it still does not quite reach the capacity of a metal in contact with the same solution.



Cesium ion inside a carbon nanotube. Blue: excess of positive charge, red: excess of negative charge.

Carbon nanotubes are of great interest for supercapacitors. Experimental and theoretical results indicate that the capacity of very small nanotubes filled with an electrolyte solution is greatly enhanced by the image interaction of the ions with the surroundings. In order to investigate this effect, we have performed DFT calculations for a cesium atom inside a thin carbon tube. The cesium atom loses an electron and forms a cation; the negative charge is distributed on the surrounding carbon rings. From the charge distribution, we can calculate the image potential experienced by the cation. This potential is a prerequisite for understanding the capacity of nanopores.

Delithation and Relithiation Kinetics of the *Olivine* Li_xFePO_4 (0<x<1) System

Steen. B. Schougaard[1]*, Christian Kuss[1], David Lepage[1],
Murielle Carmant-Dérival[1], Ngoc Duc Trinh,[1] Guoxian Liang[2]
[1)]*Université du Québec à Montréal, Département de chimie, C.P. 8888 Succ. Centre-ville, Montreal (QC) H3C 3P8, Canada*
[2)]*Clariant Canada, Inc., 280 ave. Liberté, Candiac (QC) J5R 6X1, Canada*
**Schougaard.steen@uqam.ca*

Olivine-$LiFePO_4$ is a unique member of the oxo-anion lithium transition metal class of materials that allow for relatively rapid lithium ion expulsion and uptake across the electrode surface in response to redox cycling. This combined with low cost, environmental benignity and safety has made $LiFePO_4$ a favored positive electrode material for large-scale lithium ion batteries. However, in spite of significant commercial success and a decade of intense research, the mechanism for redox cycling is still a subject of intense debate.

One challenge is the standard method used to determine redox kinetics. Specifically, the technique relies on an electrode that consists of active material, a electronic conducting filler and a binder that yield a porous structure, which is backfilled with the liquid electrolyte. This complex structure poses severe problems when attempting to derive kinetics for the individual particle, as is clearly witnessed in the available apparent diffusion coefficients, which spans several orders of magnitude. To overcome this problem we in this contribution use a chemical redox system to mimic the effect of the potential step (PITT) technique. One advantage of this approach is that the electrochemical potential *i.e.* the driving force for the reaction is delivered uniformly and simultaneously to the entire surface of the active material particles. The possible point contact bottlenecks of the standard composite electrodes are thus overcome. A further advantage of this approach is that the extracted lithium amount can be measured directly, which alleviate concerns about other parasitic electrochemical processes affecting the kinetic measurement.

The final part of the talk will target contemporary kinetic models and how these compare to our measurement.

Interactions of Pore-Forming Peptides with Lipid Films

Slawomir Sek, Joanna Juhaniewicz, Michal Jamroz, Jan Pawlowski
Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw
Żwirki i Wigury 101, 02-089 Warsaw, Poland
slasek@chem.uw.edu.pl

In medicine, there is a continuous need to overcome problems related to increasing number of multi-drug resistance pathogens. Among some other solutions, antimicrobial pore-forming peptides are often considered as an alternative to conventional drugs. It is known that their action leads to disintegration of lipid membrane and cell lysis. However, the detailed mechanisms are still unclear in many cases, especially if we consider the interactions at molecular level.

We have investigated the ability of different peptide species to interact with artificial lipid films at the air-water interface as well as on the solid support. In our studies two types of lipid films were tested, either composed of lipids found in mammals or bacteria. Such approach enables analysis of peptide action with respect to different organisms. We examined how the mode of peptide action is affected by lipid film fluidity, charge and the chemical nature of particular components. As a model antibiotic species we have used naturally occurring peptides melittin and cecropin B. The dynamics of the pore formation as well as the strength of the peptide-lipid interactions was evaluated using Langmuir technique, electrochemistry and scanning probe microscopy. Experimental findings were compared with the results of molecular dynamics simulations.

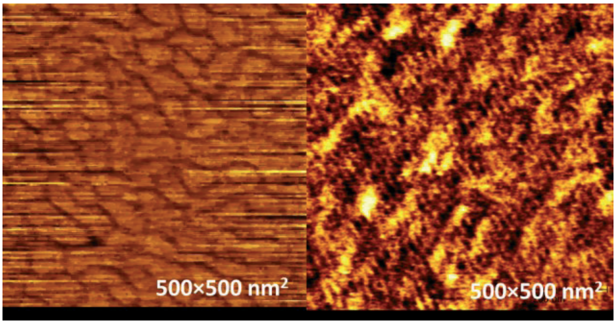


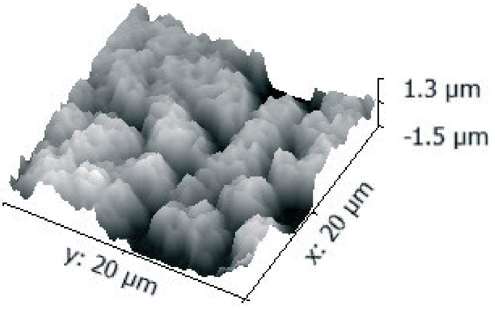
Figure 1. AFM images illustrating the change in DMPC bilayer morphology upon addition of melittin. Left: in the absence of melittin; right: in the presence of melittin.

Oral presentation

Characterizing Zinc Electrodeposits Using AFM and Scaling Analysis

Jeffrey L. Shepherd, Kirsten Swanson and Said Mahboob
Chemistry & Biochemistry Department
Laurentian University. Sudbury ON CANADA P3E 1L6
jshepherd@laurentian.ca

In the industrial method of producing high purity zinc, electrowinning is used to recover the metal at an aluminum cathode under relatively large current densities and high-deposition rates. With these conditions, electrowinning is economical but the zinc deposits are often non-uniform and sometimes cause cell short-circuits if the anode and cathode make contact. To minimize this, several leveling agents including *bone glue*, *licorice* and *sodium silicate* may be added to the zinc electrolyte to produce smoother deposits and counteract the impact of impurities. However, short-circuits are still a problem faced in many industrial operations and the development of a rapid method to characterize and predict uneven surface growth as a function of electrolyte composition is desirable. In this presentation, we discuss our studies of *Atomic Force Microscopy* (AFM) and *scaling analysis* to characterize and monitor the evolution of zinc surface roughness with electrodeposition time and electrolyte composition in a manner similarly applied to copper electrodeposits [1]. In the current study, a range of short-term zinc deposits were prepared on a polished aluminum cathode from an industrial electrolyte. The influence of the electrolyte composition and leveling agents on surface roughness was determined from three-dimensional AFM images (as shown in the figure which represents a 30 second deposit in the presence of bone glue). For a series of these images as a function of deposition time, morphological changes were quantified with scaling analysis rendering information on surface roughness, periodicity as well as the aspect ratio of surface features. The results of this analysis on short term deposits were used to determine if the method can predict the surface roughness of samples at longer deposition times. These results along with a description of the AFM and scaling procedures will be presented. [1]. T. Zhao, D. Zagidulin, G. Szymanski, J. Lipkowski. *Electrochimica Acta* **51** (2006) 2255-2260



Oxidation and Reduction Selectivity at Pt-Ru-C Sputtered Electrodes in the Presence of Methanol and Oxygen

Sayoko Shironita[1], Yuta Takahashi[1], Minoru Umeda[1,*], Mitsuhiro Inoue[2], and Takayuki Abe[2]
[1] *Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1, Kamitomioka, Nagaoka, Niigata 940-2188, Japan*
[2] *Hydrogen Isotope Research Center, University of Toyama,*
Gofuku 3190, Toyama 930-8555, Japan
**mumeda@vos.nagaokaut.ac.jp*

In this study, we describe novel Pt-Ru-C sputtered electrodes which have different reaction selectivity in the presence of methanol and oxygen. For realizing a mixed reactant fuel cell (MRFC), the anode and cathode are required to have reaction selectivity for a methanol oxidation reaction (MOR) and an oxygen reduction reaction (ORR), respectively. This is because that a mixture of methanol and oxygen is fed to each electrode in the MRFC.

Eleven Pt-Ru-C electrodes were sputter-deposited on Au substrates (ϕ8 mm) using a barrel-sputtering system by changing Ar gas pressure (0.8-3 Pa), sputtering time (20-150 min), and ac power (30-100 W) [1]. The prepared Pt-Ru-C electrodes were characterized by XRD, SEM-EDX, and XPS measurements.

As a result, two typical linear sweep voltammograms are obtained as shown in Fig. 1. Electrode 1 of Fig. 1 (upper) was prepared at 100 W for 20 min under Ar 0.8 Pa. This Electrode 1 has ORR selectivity in the presence of methanol and oxygen. On the other hand, the prepared Electrode 2 at 30 W for 35 min under Ar 3 Pa shows the MOR selectivity as seen in Fig. 1 (lower). These electrodes have almost the same composition ($Pt_{0.63}Ru_{0.30}C_{0.07}$ and $Pt_{0.63}Ru_{0.28}C_{0.08}$). Consequently, the sputtering condition enables to control the reaction selectivity in the presence of methanol and oxygen.

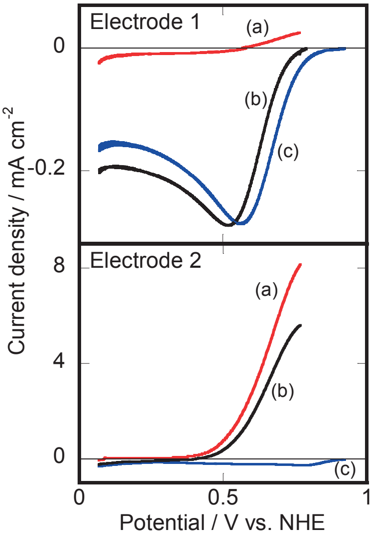


Fig. 1 Linear sweep voltammograms at Pt-Ru-C (Electrodes 1 and 2) in (a) N_2-saturated 1 M CH_3OH + 0.5 M H_2SO_4, (b) O_2-saturated 1 M CH_3OH + 0.5 M H_2SO_4, and (c) O_2-saturated 0.5 M H_2SO_4. Sweep rate: 10 mV s^{-1}.

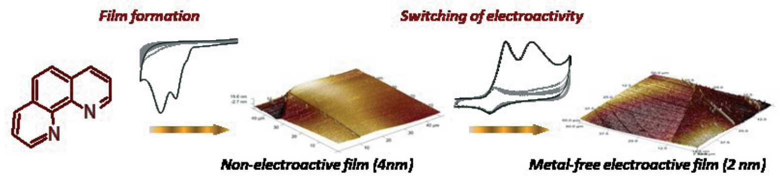
[1] T. Abe, S. Akamaru, K. Watanabe, Y. Honda, J. Alloys Comp., 402 (2005) 227-232.

Formation of Ultrathin Electroactive Film on Carbon Surface from 1,10-Phenantroline in Acidic Electrolyte

Galyna Shul, Daniel Bélanger
Département de Chimie, Université du Québec à Montréal
CP8888, Succ. Centre-Ville, Montréal, Québec, Canada H3C 3P8
galyna.shul@gmail.com

The deliberate modification of electrode surfaces by covalently attached molecules has received extensive interest due to their versatile application in the field of microelectronics technology, energy storage and conversion, chemical and biochemical sensing and catalysis.[1,2] One of the functionalization techniques available for the electrode surface modification is electropolymerization and self-limiting electrodeposition of non-conducting polymers, in particular, that provides thin (<100 nm) conformal deposits.[3,4]

Herein, we show that 1,10-phenanthroline in aqueous acid solution undergoes electrochemical reduction that leads to formation of ultrathin (<4 nm) non-conducting and non-electroactive film covalently bonded to the carbon electrode surface. The electroactivity is switched on, when the modified electrode is treated by the following electrochemical oxidation (Scheme 1). The chemical structure and morphology of electrodeposited films were examined by time-of-flight secondary ion mass spectrometry, X-ray photoelectron spectroscopy, electrochemical techniques, and by atomic force microscopy.



Scheme 1. Graphic presentation of pyrolized photoresist film surface modification by electrochemical treatment in 1,10-phenanthroline aqueous acid solution.

(1) Bélanger, D.; Pinson, J. *Chem. Soc. Rev.* **2011**, *40*, 3995.
(2) McCreery, R. L. *Chem. Rec.* **2012**, *12*, 149.
(3) Fischer, A. E.; McEvoy, T. M.; Long, J. W. *Electrochim. Acta* **2009**, *54*, 2962.
(4) Hu, D.; Peng, C.; Chen, G. Z. *ACS Nano* **2010**, *4*, 4274.

Electrocatalytic properties of RuO_2 nanocomposite for hydrogen evolution reaction

M.V. Sivaiah, D. Abirami, H.G. Ang
*Energetics Research Institute (E**n**RI), Nanyang Technological University,*
Block N1-B4a-02, Nanyang Avenue, NTU, Singapore 639798
Tel : (65) 6513 2756; Fax: (65) 6792 7173; MVSivaiah@ntu.edu.sg

Hydrogen evolution reaction (HER) through proton-combination or water-splitting was one of the most sorted electrochemical technologies (water electrolyzer, chlor-alkali/chlorate process, etc). In contrast to chemically reduced oxides under HER conditions, ruthenium oxide (RuO_2) emerged as electrocatalyst for HER with more stability even under poisoning of metals [1-3]. RuO_2 is known for good conducting metal oxide with combination of electronic and protonic conductivity. It was reported that hydrous ruthenium oxide ($RuO_2.nH_2O$) is a nanocomposite consists of dispersed rutile-like nanocrystals with water at the boundaries [4]. Electronic conductivity of RuO_2 arises due to crystals and protonic conductivity through structural water bounded to crystals [4].

In general, RuO_2 based electrodes were prepared by thermal decomposition of chloride salts and resulted material mostly represents the anhydrous RuO_2. In case of RuO_2 synthesized through chime-douce method, a proper calcination is needed in order to have particular structural water content for exhibiting better electro-catalytic activity and such studies were existed only for RuO_2 application in supercapacitors, O_2 and Cl_2 evolution reactions. To investigate the electrocatalytic activity of hydrous RuO_2 towards HER, RuO_2 nanocomposites were synthesized by ion-exchange method at room temperature. Calcined and un-calcined specimens were made as ink consists of nafion® 117 and evaluated for HER in 1M NaOH and 0.5M H_2SO_4 medium in three electrode electrochemical cell. RuO_2 nanocomposite consists of moderate structural water content shown high activity for HER in basic and acidic medium, when compared to hydrous or anhydrous RuO_2 and these results are different when compared to data obtained for O_2 or Cl_2 evolution activity over hydrous / anhydrous RuO_2. Physico-chemical characterization data will be presented to describe the RuO_2 nanocomposites electrocatalytic activity towards HER.

References

1. H. Over, Chem. Rev., 112 (2012) 3356.
2. E. R. Kötz, and S. Stucki, J. Appl. Electrochem. 17 (1987) 1190.
3. E. Fachinotti, E. Guerrini, S. Trasatti, J. Electroanal. Chem., 600 (2007) 103.
4.W. Dmowski, T. Egami, K.E. Swider-Lyons, C.T. Love and D.R. Rolison, J. Phys. Chem. B, 106 (2002) 12677.

SPM studies of intercalation mechanisms in electrode materials for Li-ion batteries at the nanoscale

Lukas Seidl, Jiwei Ma, Oliver Schneider, Ueli Heiz, Ulrich Stimming
Technische Universität München, 85747 Garching, Germany
Email: stimming@tum.de

Rechargeable lithium-ion batteries have been significantly advanced and successfully commercialized in the past two decades, particularly in the areas of portable and mobile applications. Nowadays, the advancement of hybrid electrical vehicles (HEVs) and electrical vehicles (EVs) technologies depends strongly on the availability of Li-ion battery systems improved with respect to cyclability and energy density [1]. There will be a great demand of batteries for transportation applications as well as for the development and implementation of affordable, reliable and safe energy storage systems to support and reinforce the ambitious renewable energy research in smart grids. This raises big challenges for the next generation rechargeable batteries concerning cost, safety, power and energy density, cycle life, etc [2].

The optimization of energy and power density, as well as cycle life of energy storage systems requires developing a better understanding of solid-state electrochemical mechanisms on nano-, micro- and macro-scales. Indeed, the classical electrochemical techniques, such as cyclic voltammetry and electrochemical impedance spectroscopy, are clearly limited at the nanoscale. Therefore, various scanning probe microscopy (SPM) studies have been devoted to investigate the nanoscale electrochemical reactions and the physical basis of imaging mechanisms [3]. In virtue of the electrochemical STM (ECSTM) technique, we started from a specific model graphite, HOPG, to obtain a deep understanding and accurate prediction of reaction mechanisms for the anode side of rechargeable Li-ion batteries. In order to analyze the intercalation mechanisms of Li^+, topographical changes of HOPG were analyzed in 1 M $LiPF_6$ in EC/DMC (v/v=1:1) under stepwise polarization to different potentials by ECSTM. The observed changes are contributed from the intercalation of Li^+ into HOPG when polarization potential is at and below 0.9 V vs. Li^0/Li^+. The results will be described in terms of the combination between physicochemical phenomena and electrochemical metal ion intercalation into single-crystalline host structures comparing different electrolyte systems and metal ions. The achieved knowledge will be further used as model study for other investigations, i.e. oxide-based electrode materials for rechargeable batteries technologies.

References:
[1] J. M. Tarascon, M. Armand, Nature 414 (2001) 359
[2] J. B. Goodenough, Y. Kim, Chem. Mater. 22 (2010) 587
[3] S. V. Kalinin, N. Balke, Adv. Mater. 22 (2010) E193

Physicochemical Characterization of DNA Films on Gold Surface Containing Nucleotides of Different-Length

Anna M. Nowicka, Edyta Matysiak, Slawomir Sek, Zbigniew Stojek
University of Warsaw, Faculty of Chemistry
Pasteura 1, 02-093 Warsaw, Poland
e-mail address: stojek@chem.uw.edu.pl

Films of single stranded- or double stranded DNA immobilized at the electrode surface play a very important role in biotechnological and biomedical applications including DNA microarrays, biosensors, and studies of DNA-drug interactions. DNA film can be attached to the gold substrate chemically or physically.

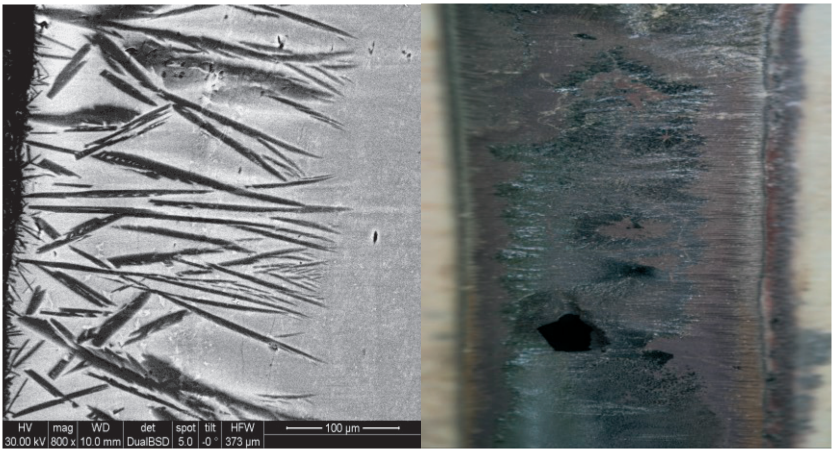
The simplest method to immobilize DNA film with parallel orientation of the strands at a gold surface is its adsorption at a controlled potential. However, this procedure leads to the existence of multiple contacts of the noncovalently bound DNA strands with the gold surface. In such the case the accurate measurement of the DNA surface coverage, a crucial parameter for the quantitative description of the interactions, is really difficult. The absolute quantification of DNA strands in the film is possible only by application of radiolabeling method, but the conditions of such experiments are rather hazardous and also the hazardous waste disposal is very problematic. The label-less DNA film characterization is possible by applying such techniques as surface plasmon resonance or elipsometry. However, the presence of non-specific adsorption substantially complicates the data interpretation. Fortunately X-ray photoelectron spectroscopy and quartz crystal microbalance can also provide this type of information.

We report here on how electrochemical quartz crystal microbalance (EQCM), electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM) and UV-Vis spectroscopy can be used together for physicochemical quantitative and qualitative characterization of DNA films on gold substrates. In the experiments we used synthetic oligonucleotides of different length. Applying the nucleotides of different length allowed us to get the information on how the number of nucleotides in the chain affects the quality of the formed DNA layer and in consequence the electrooxidation of DNA guanine. The accumulation of DNA on the gold electrode surface was done by adsorption at a constant potential. The conditions for deposition of DNA were optimized to get a satisfying agreement between the data, and particularly the electrode coverage, obtained by the employed methods.

Influence of the electrochemical reaction between the components of the gas phase and the oxide melt on the structure of oxide systems

Suleimenov E.N
Kazakh British Technical University
Tole by str 59, of 219 Almaty, 050 000
Republic of Kazakhastan
e-mail metallaim@mail.rus

We have studied the influence of the unsteady electric current on the electrochemical reaction between the oxide melt and the various components of the gas phase (carbon monoxide, carbon dioxide, argon and various mixtures of these gases).Experiments were carried out on a synthetic slag of composition as follows, %: SiO_2 38.70; Al_2O_3 10.38; $Fe_{\text{total oxides.}}$ 35.92; CaO 14.55; analysis discrepancy +1.65. Experiments were carried out at 1250 ^{0}C temperature while slag melting point was 1220^{0}C. It was found that the unsteady electric current causes a chemical reaction between all the components of the gaseous phase (including argon), which leads to considerable changes in the structure of the melt. The electrochemical reaction causes crystallization of the melt to form various chemical compounds. An example is a photo macrocyclization and microcrystallization melt. In some cases there is an analogy between the form of micro (left) and macro (on the right) crystals. This is seen in the above pictures.



Applications of Atomic Layer Deposition for Li Ion Batteries

Jian Liu[1], Xifei Li[1], Mei Cai[2], Andy Xueliang Sun[1]*
[1]*The University of Western Ontario, London, ON N6A 5B8, Canada*
[2]*General Motors R&D Center, Warren, 48090-9055, MI, USA*
**Presenting author: xsun@eng.uwo.ca*

Atomic layer deposition (ALD) is a novel and unique coating technique with many applications in energy storage and conversion [1]. In this talk, we will present our recent work on exploring the applications of atomic layer deposition (ALD) in both fuel cells and Li ion batteries [2-6].

We will focus on employing ALD as a surface-modification method to enhance the performance of LIBs. Different materials for surface-modification (such as Al_2O_3, ZrO_2, TiO_2 and $AlPO_4$) [2,3] were first developed by ALD. Then systemic studies were carried out by using those materials to modify the anode ($Li_4Ti_5O_{12}$, SnO_2) [4] and the cathode (commercial $LiCoO_2$, NMC) [5]. The effects of different coating materials on the LIB performance of the anode and cathode were investigated in details. In addition, the potential application of ALD as a powerful technique for preparing solid-state electrolyte will be demonstrated [6]. We will discuss further development of ALD for Li ion batteries.

Keywords: Atomic Layer Deposition, Graphene, Li ion Batteries

Reference:

[1] X. Meng, X.-Q. Yang, X. Sun. ***Adv. Mater.*** 2012, 24, 3589-3615.

[2] J. Liu, X. Meng, Y. Hu, D. Geng, M.N. Banis, M. Cai, R. Li, X. Sun. ***Carbon*** 2013, 52, 74-82.

[3] J. Liu, Y. Tang, B. Xiao, T.K. Sham, R. Li, X. Sun. ***RSC Adv***. 2013, 3, 4492-4495.

[4] X. Li, X. Meng, J. Liu, D. Geng, Y. Zhang, M. Banis, Y. Li, R. Li, X. Sun, M. Cai, M. Verbrugge, **Adv. Funct. Mater.** 22 (2012) 1647-1654.

[5] X. Li, J. Liu, M. Banis, A. Lushington, R. Li, M. Cai, X. Sun, **Energy Environ. Sci.** (2013) In press.

[6]. J. Liu, M. Banis, X. Li, A. Lushington, M. Cai, R. Li, T.-K. Sham, X. Sun, **J. Phys. Chem. C** 117 (2013) 20260-20267

Oral presentation

Efficient Oxygen Reduction Reaction on N-doped Graphene Nanoribbons: a Combined Theoretical and Experimental Study

Chia-Liang Sun [a,*], Jin-Ting Tsai [a], Yuan-Han Huang [a], Chun-Yi Chiu [a], Po-Tuan Chen [b], and Michitoshi Hayashi [b]
a *Department of Chemical and Materials Engineering, Chang Gung University, Kwei-Shan, Tao-Yuan 333, Taiwan*
b *Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan*
e-mail address: sunchialiang@gmail.com

Recently we demonstrated the synthesis of graphene oxide nanoribbons (GONRs) from the facile unzipping of multiwalled carbon nanotubes (MWCNTs). [1, 2] In this study the N-doped graphene nanoribbons (NGNRs) for oxygen reduction reaction (ORR) will be investigated both theoretically and experimentally. The calculations of O_2 molecule and dissociated oxygen atoms adsorbing on N-doped graphene nanoribbon models using density functional theory were performed. N dopants at zigzag or armchair N-doped graphene nanoribbon models have unique adsorption energies with O_2 molecule and dissociated oxygen atoms. The substitutional N atom with a nearby vacancy defect exhibits the most strong adsorption abilities and so be viewed as the most possible candidate for ORR application. On the other hand, well-behaved ORR curves can be obtained using NGNR electrode alkaline KOH and neutral phosphate buffered saline (PBS) solutions, respectively. In summary, this novel nanocarbon material, NGNR, is believed to be an efficient cathode catalyst for a biofuel cell.

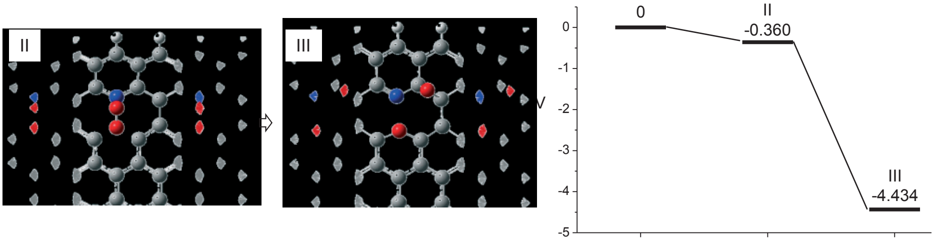


Figure 1. Relative energy of one O_2 molecule (II state) and dissociated oxygen atoms (III state) on a pyridinic-type NGNR model. (C, N, O and H atoms are gray, blue, red and white spheres, respectively.)

References

[1] Sun, C. L., Chang, C. T., Lee, H. H., Zhou, J., Wang, J., Sham, T. K., Pong, W. F. ACS Nano 5 (2011) 7788-7795.

[2] Lin, L. Y., Yeh, M. H., Tsai, J. T., Huang, Y. H., Sun, C. L., Ho, K. C. J. Mater. Chem. A 1 (2013) 11237-11245.

Electrochemical in situ FTIR spectroscopic studies of adsorption processes on Pt single crystal planes and nanoparticles

Chang-Deng Xu, Jin-Yu Ye, Ling Chen, Chun-Hua Zhen, Zhi-You Zhou and Shi-Gang Sun*
State Key Lab of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
E-mail: sgsun@xmu.edu.cn

Adsorption processes of molecules including small organic fuels, functional molecules such as surfactants, stabilizers etc. are key steps in electrocatalysis and shape-controlled synthesis of nanoparticle catalysts with well-defined surface atomic arrangement. The electrochemical in situ FTIR spectroscopy allows to characterize, at a molecule level, adsorbates and interaction of molecules with electrode, thus provides profound understanding on the mechanism of electrocatalysis and shape-control growth of nanoparticles. This communication reports our recent results concerning following 3 aspects: (1) Co-adsorption processes of CO and CN^- on Pt(100) and Pt(110) electrodes. As CO species are commonly generated from dissociative adsorption of small organic fuels and function as both intermediates and poisoning species, the study revealed essential interaction between CO and CN^- on different atomic arrangements of Pt single crystal surfaces. (2) Interaction of functional molecules with Pt single crystal planes. The functional molecules such as CTAB, PVP play a key role in controlling the surface structure/shape of metal nanoparticles in shape-controlled synthesis. In situ FTIR spectroscopic investigation has provided valuable information in understanding the mechanism of shape-controlled synthesis of Pt nanocatalysts enclosed with well-defined single crystal facets. (3) Electrocatalytic processes of ethanol on Pt nanocatalysts with high-index-faceted structure. The Pt nanocatalysts of high-index facets exhibit a high activity for ethanol oxidation. In situ FTIR results revealed that the Pt nanoparticles enclosed with high-index facets possess a high reactivity of breaking the C-C bond than commercial Pt catalysts.

Acknowledgements. Financial supports from NSFC (grants: 21021002, 21229301 and 21361140374) are highly acknowledged.

One-dimensional Pt Nanostructured Electrocatalysts for PEM Fuel Cell Applications

Shuhui Sun[1,2,*], Gaixia Zhang[1,2], Mei Cai[3], Ruying Li[2], Jean-Pol Dodelet[1],
Xueliang Sun[2,*]
[1]Institut national de la recherche scientifique (INRS)-Énergie, Matériaux, Télécomm.
1650 Boulevard Lionel-Boulet, Varenne, Quebec, J3X 1S2, Canada
[2]Department of Mechanical and Materials Engineering, the University of Western Ontario, London, Ontario, N6A 5B9, Canada
[3]General Motors Research & Development Center, Warren, MI, 48090-9055, USA
**E-mail address: shuhui@emt.inrs.ca (S Sun) or xsun@eng.uwo.ca (X Sun)*

PEM fuel cells (PEMFCs) are expected to play dominant role in future clean energy solutions for various applications. However, short life-time and high cost of Pt catalyst are the main obstacles for the commercialization of PEMFCs. Very recently, one-dimensional (1D) structures of Pt, such as nanowires (NWs), have emerged as a new type of promising fuel cell catalyst, exhibiting much enhanced activity and stability compared to the commercially-used Pt/C nanoparticle catalysts. Here, I will systematically introduce our recent work on 1D Pt NWs for fuel cells, including: (i) A facile method to synthesize Pt NWs (4 nm in diameter), which exhibit 3-times better activity and 5-fold better durability than the state-of-the-art commercial catalyst made of Pt nanoparticles;[1-3] (ii) PtNWs on Sn@CNT nanocable 3D electrode with much enhanced performance in ORR, MOR, and CO tolerance;[4] (iii) Diameter control of Pt NWs grown on CNTs and N-doped CNTs.[5,6]

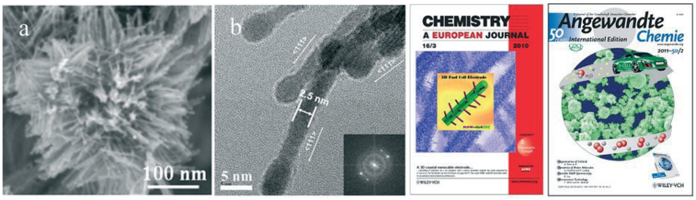


Fig. (a) Pt NWs (D= 4 nm); (b) ultrathin Pt NWs (D=2.5 nm); (c) PtNW-Sn@CNT; (d) Pt nanostars.

1. Sun, S. H., Yang, D. , Villers, D., Zhang, G., Sacher, E., Dodelet. J. P. (2008) *Adv. Mater.*, 20, 571.
2. Sun, S. H., Jaouen, F., Dodelet, J. P. (2008) *Adv. Mater.,* 20, 3900.
3. Sun, S. H., Zhang, G. X., Geng D., Chen, Y., Li. R., Cai, M., Sun, X. L. *Angew. Chem. Int. Ed.,* 50 (2011) 422. (VIP+ Cover)
4. Sun, S. H., Zhang, G., Geng, D., Chen, Y, Li, R, Cai, M., Banis, M., Sun, X. L. (2010) *Chemistry-A European Journal,* 16, 829. (Inside Cover).
5. Sun, S. H., Yang, D., Zhang, G., Sacher, E., Dodelet. J. P. (2008) *Chem. Mater.,* 19, 6376.
6. Sun, S. H., Zhang, G., Zhong, Y., Liu, H., Li, R., Zhou, X., Sun, X. (2009) *Chem. Commun.,* 45, 7048.

Self-Assembled Gold Nanoparticles as Nanelectrocatalyst Templates for Surface Nanostructuring

A. Taleb[a], X. Yanpeng[a], P. Dubot[b]
[a] *UPMC - Laboratoire d'Electrochimie, Chimie des Interfaces et Modélisation pour l'Energie ENSCP, Chimie ParisTech, CNRS/UMR 7575.11 rue P. et M. Curie, 75231 Paris cedex 05 France*
[b] *Institut de chimie et des matériaux Paris Est UMR 7181, 2-8 rue Dunant F-94320 Thiais-France*
Abdelhafed.taleb@upmc.fr

We report a selective growth method of metallic (Cu, Ag, Co) nanoparticles electrodeposition on hexagonally patterned electrodes by self-assembled gold nanoparticles (Au NPs) [1,2]. The self-assembled Au NPs behave as an ensemble of electrocatalysis seed layer for Cu electrodeposition. Au NPs activate the inhibited site (without defects) of bare HOPG for the same applied potential. This result is explained by the mechanical strain of Au NPs on graphene inducing the enhancement of their adsorption and catalytic activity [3]. The dodecanethiol ligands around the Au NPs fix the distance between them and avoid the coalescence processes in the first electrodeposition stage. The hexagonal periodicity of the Au NPs is well reproduced. This nanostructuring method provides a promising way to control the electrodeposits growth into ordered structure at nanometre resolution.

References

[1] A. Taleb, C. mangeney, V. Ivanova J. Electrochem. Soc. 158 (2011) K28-K34.
[2] A. Taleb, X. Yanpeng, P. Dubot, J. Electroanal. Chem. 693 (2013) 60–66
[3] M. Zhou, A. Zhang, Z. Dai, Y. P. Feng, C. Zhang, J. Phys. Chem. C 114 (2011) 6541-16546.

Oxygen Reduction on Fe_3O_4 nanoparticles supported on Printex Carbon and on Graphene

Ana C. Tavares[a], Willyam R. P. Barros [b], Shuhui Sun[a], Marcos R. V. Lanza [b]
[a]*INRS – Énergie, Matériaux et Télécommunications*
1650 Boulevard Lionel-Boulet, Varennes, Québec, Canada, J3X 1S2
[b]*GPEA, Instituto de Química de São Carlos, Universidade de São Paulo, Av. Avenida João Dagnone, 1100 - Jardim Santa Angelina- São Carlos - SP – Brazil*
ana.tavares@emt.inrs.ca

Magnetic nanoparticles are being studied and developed for various technological applications including biomedicine, bioengineering and electrochemistry. Here we report our recent results on (i) unsupported, supported on (ii) Printex Carbon and (iii) on graphene Fe_3O_4 nanoparticles, focusing on the oxygen reduction reaction (ORR) in alkaline medium. The nanoparticles were synthesized using a simple co-precipitation method and characterized for their crystal structure and textural properties by TEM and SAED. The effect of the nature of the carbon support on their electrocatalytic activity towards ORR was evaluated by Cyclic and Linear Voltammetries. As shown in Figure 1a, smaller oxide nanoparticles were synthesized on graphene. As expected the electrocatalytic activity towards ORR increased from unsupported to supported nanoparticles with a shift of the half way potential of about 240 mV, Figure 1b. The influence of the oxide loading, oxide particle size and of the nature of carbon support on the ORR will be discussed in detail.

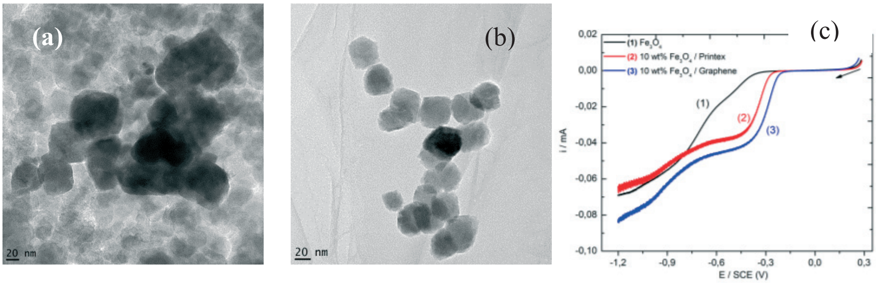


Figure 1. TEM images of 10 wt% Fe_3O_4 nanoparticles supported on (a) Printex and (b) graphene; (c) Linear voltammograms recorded in O_2 saturated KOH 1M at 10 mVs^{-1} and 1600 rpm.

Acknowledgements: FAPESP (2011/06681-4; 2013/06682-6), CQMF (Québec, Canada) and CRNSG (Canada).

Self-Assembled Gold Nanoparticles as Nanelectrocatalyst Templates for Surface Nanostructuring

A. Taleb[a], X. Yanpeng[a], P. Dubot[b]
[a] *UPMC - Laboratoire d'Electrochimie, Chimie des Interfaces et Modélisation pour l'Energie ENSCP, Chimie ParisTech, CNRS/UMR 7575.11 rue P. et M. Curie, 75231 Paris cedex 05 France*
[b] *Institut de chimie et des matériaux Paris Est UMR 7181, 2-8 rue Dunant F-94320 Thiais-France*
Abdelhafed.taleb@upmc.fr

We report a selective growth method of metallic (Cu, Ag, Co) nanoparticles electrodeposition on hexagonally patterned electrodes by self-assembled gold nanoparticles (Au NPs) [1,2]. The self-assembled Au NPs behave as an ensemble of electrocatalysis seed layer for Cu electrodeposition. Au NPs activate the inhibited site (without defects) of bare HOPG for the same applied potential. This result is explained by the mechanical strain of Au NPs on graphene inducing the enhancement of their adsorption and catalytic activity [3]. The dodecanethiol ligands around the Au NPs fix the distance between them and avoid the coalescence processes in the first electrodeposition stage. The hexagonal periodicity of the Au NPs is well reproduced. This nanostructuring method provides a promising way to control the electrodeposits growth into ordered structure at nanometre resolution.

References

[1] A. Taleb, C. mangeney, V. Ivanova J. Electrochem. Soc. 158 (2011) K28-K34.
[2] A. Taleb, X. Yanpeng, P. Dubot, J. Electroanal. Chem. 693 (2013) 60–66
[3] M. Zhou, A. Zhang, Z. Dai, Y. P. Feng, C. Zhang, J. Phys. Chem. C 114 (2011) 6541-16546.

Oxygen Reduction on Fe_3O_4 nanoparticles supported on Printex Carbon and on Graphene

Ana C. Tavares[a], Willyam R. P. Barros [b], Shuhui Sun[a], Marcos R. V. Lanza [b]
[a]INRS – Énergie, Matériaux et Télécommunications
1650 Boulevard Lionel-Boulet, Varennes, Québec, Canada, J3X 1S2
[b]GPEA, Instituto de Química de São Carlos, Universidade de São Paulo, Av.
Avenida João Dagnone, 1100 - Jardim Santa Angelina- São Carlos - SP – Brazil
ana.tavares@emt.inrs.ca

Magnetic nanoparticles are being studied and developed for various technological applications including biomedicine, bioengineering and electrochemistry. Here we report our recent results on (i) unsupported, supported on (ii) Printex Carbon and (iii) on graphene Fe_3O_4 nanoparticles, focusing on the oxygen reduction reaction (ORR) in alkaline medium. The nanoparticles were synthesized using a simple co-precipitation method and characterized for their crystal structure and textural properties by TEM and SAED. The effect of the nature of the carbon support on their electrocatalytic activity towards ORR was evaluated by Cyclic and Linear Voltammetries. As shown in Figure 1a, smaller oxide nanoparticles were synthesized on graphene. As expected the electrocatalytic activity towards ORR increased from unsupported to supported nanoparticles with a shift of the half way potential of about 240 mV, Figure 1b. The influence of the oxide loading, oxide particle size and of the nature of carbon support on the ORR will be discussed in detail.

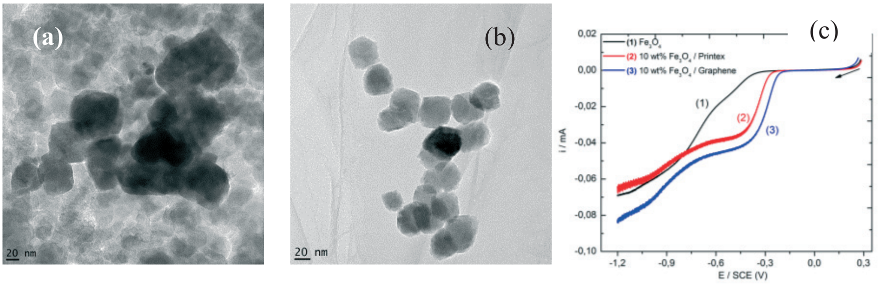


Figure 1. TEM images of 10 wt% Fe_3O_4 nanoparticles supported on (a) Printex and (b) graphene; (c) Linear voltammograms recorded in O_2 saturated KOH 1M at 10 mVs^{-1} and 1600 rpm.

Acknowledgements: FAPESP (2011/06681-4; 2013/06682-6), CQMF (Québec, Canada) and CRNSG (Canada).

Some Developments and Bottlenecks of Electrochemical Surface Raman Spectroscopy

Zhong-Qun Tian
State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
zqtian@xmu.edu.cn

The field of surface-enhanced Raman spectroscopy (SERS) was initiated in 1974 [1, 2]. In the past four decades SERS has gone through a tortuous pathway to develop into a powerful diagnostic technique [3-6]. I'll first give a brief introduction about the early history with particular emphasis of the importance of challenging the textbooks and authorities for opening up a new scientific field.

Based on three factors: detection sensitivity, resolution (energetic, spatial and temporal) and generality (materials, morphological and molecular), I'll discuss development bottlenecks of electrochemical Raman spectroscopy. Some thoughts on how to remove each one will be presented for the future development.

1) Characterizing weak interactions between adsorbates, ions, solvents and electrode surfaces.
2) Pushing sensitivity toward the detection limit with new instruments and tools.
3) Correlating spectroscopic and electrochemical data with micro- or nano-electrodes.
4) Catching reaction intermediates by pump-probe or other new methods.
5) Probing solid-solid interfacial dynamics in-situ.
6) Hyphenating several techniques with 2D or 3D correlated spectroscopies.
7) Combining experimental and theoretical approaches.

References

[1]. M. Fleischmann, P. J. Hendra and A. J. McQuillan, Chem. Phys. Lett., 26, 163 (1974).
[2]. D. L. Jeanmaire and R. P. Van Duyne, J. Electroanal. Chem., 84, 1 (1977).
[3]. D.Y. Wu, J.F. Li, B. Ren, Z.Q. Tian, Chem. Soc. Rev., 37, 1025-1041 (2008)
[4]. J.F. Li, et. al. , Nature, 464, 392-395 (2010).
[5]. S.Y. Ding, X.M. Zhang, B. Ren, Z.Q. Tian, SERS: General Introduction, Encyclopedia of Analytical Chemistry, (2013).

Acknowledgement: This project was supported by NSFC (21021002, 21033007 and 21153003) and MOST (2011YQ030124) .

In situ SEIRAS Investigation of Methanol Oxidation Reaction on PtRu Alloy and Ru@Pt Core-Shell NPs: New Insights on an Old Story

Dianne O. Atienza[1], DeJun Chen[1], Thomas C. Allison[1], and YuYe J. Tong[1],
Department of Chemistry, Georgetown University
37th & O Streets, NW, Washington DC 20057, USA, [2]Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8320, Gaithersburg, MD, 20899-8320, USA
yyt@georgetown.eu

Methanol oxidation reaction (MOR) on PtRu surfaces has been subjected to intensive investigations over the last decades[1] and bi-functional mechanism proposed by Watanabe et al. in 1975[2] has been the standard rationalization of the much improved CO poisoning tolerance observed on the PtRu as compared to the pure Pt surfaces. It is also well known that the MOR can also follow either of the so-called indirect and direct reaction pathways of which the former leads to the formation of the poisoning CO[3]. However, how the latter can be enhanced as a CO-poisoning free reaction pathway for practical use in methanol fuel cells has been much less studied. In this presentation, we will discuss some new mechanistic insights gleaned from our *in situ* SEIRAS[4] (surface enhanced IR reflection absorption spectroscopy) investigation of the MOR on PtRu alloy and Ru@Pt core-shell nanoparticles (NPs), particularly in the <0.3V (vs. RHE) electrode potential region within which no CO oxidation can occur. We will show that in the case of PtRu alloy NPs, the widely used multi potential cycles can be optimized for MOR activity if the up potential limit is set to be less than 0.8V and leads to the formation of segregated Pt and Ru surface configuration. In the case of Ru@Pt NPs, we will discuss the experimental evidence indicating that there exists an optimal Pt coverage at which no CO was generated during the MOR but still with much enhanced activity as compared to pure Pt.

1. Sharma, S.; Pollet, B. G. *J. Power Sources* **2012**, *208*, 96.
2. Watanabe, M.; Motoo, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 267.
3. Housmans, T. H. M.; Wonders, A. H.; Koper, M. T. M. *J. Phys. Chem. B* **2006**, *110*, 10021.
4. Osawa, M.; Ataka, K.; Yoshii, K.; Yotsuyanagi, T. *J. Elect. Spectr. Rel. Phenom.* **1993**, *64*, 371.

Electrochemistry of hybrid TiO_2/PANI thin films employing ionic liquids as electrolytes

R. A Fernández, T. M. Benedetti, F. E. Reis, P. H. C. Camargo, R. M. Torresi*
*Instituto de Química-Universidade de São Paulo, Av Prof. Lineu Prestes 748 – São Paulo – SP – Brasil *rtorresi@iq.usp.br*

Nanostructured materials have attracted great interest in recent years because of their particular mechanical, electrical and optical properties. In electrochemical energy storage devices, like batteries and supercapacitors, the control of the synthesis and properties of nanostructured materials are becoming increasingly important [1].

Titanates have being intensively investigated as anodes for lithium-ion batteries due to their superior safety and high capacity to store charge compared with graphite [2].

Conducting polymers can form hybrid structures with nanostructured oxides, offering an alternative pathway for the access of the lithium ion and also higher ion diffusion rates as well as higher electronic conductivity [3].

Furthermore, the progress in lithium-ion batteries is a multi-faceted challenge that depends on the improvements in the electrodes materials and also in the electrolyte properties [1]. In this sense, ionic liquids (ILs) can present an impact on energy technologies due to its intrinsic ionic conductivity and high chemical and electrochemical stability [4].

In this work, hybrid thin films composed of titanium dioxide (TiO_2) and polyaniline (PANI) as a binder, were prepared and investigated for application as anode in energy storage devices using different ionic liquids based electrolytes. TiO_2 nanoparticles were deposited by pulsed electrophoresis from a colloid suspension and PANI was successively electrodeposited by cyclic voltammetry employing an acid aniline solution. The nanospheres of TiO_2 presented a uniform distribution over the electrode surface and PANI was located at the boundaries of the spheres. By comparing with the film containing only the oxide, similar morphology and enhanced electrochemical activity were obtained when PANI films were grown over the TiO_2.

Electrochemical quartz crystal microbalance with Dissipation (EQCM-D) data, combined with cyclic voltammetry was used to study the ionic exchange process in modified electrodes using ILs as electrolytes. The analysis of the ionic exchange in TiO_2 electrodes have shown that charge compensation is achieved predominantly by lithium; nevertheless in hybrid electrodes both anions and cations are involved in the charge compensation process, depending on the nature of the ionic liquid, the number of voltammetric cycles and the employed scan rate.

Low-Cost Molybdenum Sulfide and Carbide Catalysts for Hydrogen Evolution

Sami Tuomi, Tanja Kallio
Research Group of Electrochemical Energy Conversion and Storage, Department of Chemistry, Aalto University
P.O. Box 16100, 00076 Aalto, Finland
sami.tuomi@aalto.fi

Platinum is widely used to catalyze hydrogen evolution reaction but it is expensive material and it is not abundantly available. For these reasons lots of work has concentrated to develop and search for alternative catalyst materials. Molybdenum based materials are interesting option due to the low price and high availability. Molybdenum carbide and sulfide were chosen as the catalyst for this research due to commercial availability and their expected catalytic activity towards hydrogen evolution. The catalytic activities of these materials were researched with rotating disc electrode (RDE) and in a methanol electrolysis cell. The RDE experiments reveal that on-set potentials for the hydrogen evolution are really low for both catalysts. For the MoS_2 the reaction starts right after the potential has passed under 0 V, although the activity is quite moderate until the potential reaches -0.3 V where there is a significant increase in the activity. The methanol electrolysis cell experiments (Fig. 1) show that cells with these catalysts can produce reasonable amount of hydrogen even with low potentials. Also the performance is stable over time and even increase in the hydrogen production is observed with MoS_2. The increased activity is due to increase in the number of active sites where the reaction can occur. This is due to modification of the catalyst structure resulting in a higher surface area. In the cell experiments Mo_2C showed activity which is significantly higher than with the MoS_2 though both catalysts show promising performance. The results prove that these catalysts are efficient in a real application and they are potential substituents for platinum as a hydrogen evolution catalyst.

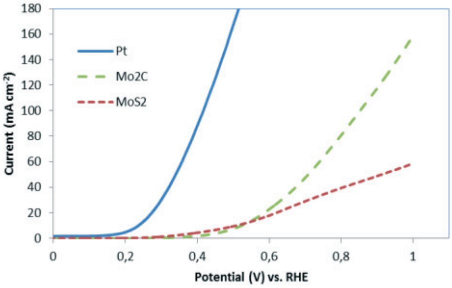


Fig. 1. The methanol electrolysis cell dependency of voltage catalysts at 70 °C.

H_2O_2 and Fe^{2+}-Induced Pt Electrode Dissolution in H_2SO_4 Solution

Minoru Umeda,* Hayato Itaya, and Sayoko Shironita
Dept. of Materials Science and Technology, Nagaoka University of Technology
1603-1, Kamitomioka, Nagaoka, Niigata 940-2188, Japan
**mumeda@vos.nagaokaut.ac.jp*

In this report, we describe Pt electrode dissolution induced by H_2O_2 and Fe^{2+} in H_2SO_4 solution. Pt-based electrodes used in polymer electrolyte fuel cells (PEFCs) deteriorate during a long-term power generation. This is probably because that unordinary circumstance arisen in the PEFC accelerates the Pt dissolution. Especially, H_2O_2 as a by-product of O_2 reduction reaction and some metal-ion contaminations are the candidates. An electrochemical quartz crystal nanobalance (EQCN) was employed to evaluate the Pt weight loss under the electrode potential change. It was found that the addition of Fe^{2+} further increases the Pt dissolution amount in the presence of H_2O_2.

The Pt dissolution was measured by EQCN (QCN: QCM922, 9 MHz; potentiostat: Model 283; Princeton Applied Research) in 0.5 mol dm^{-3} H_2SO_4. The measurements were performed using ϕ5 mm Pt-EQCN electrode as a working, Pt plate as a counter, and Ag/Ag_2SO_4 as a reference electrode.

In Fig. 1, typical cyclic voltamograms are seen, and any influence of Fe^{2+} addition is not obvious. Figure 2 shows the weight change of the Pt electrode by a potential step. The Pt mass change hardly occurs in the 0.5 mol dm^{-3} H_2SO_4. In contrast, the Pt electrode mass decreases with the potential step by an addition of 294 mmol dm^{-3} H_2O_2. Moreover, only 10 mmol dm^{-3} Fe^{2+} addition increases the Pt dissolution. These results strongly suggest that the Fe^{2+} catalytically affects the H_2O_2 decomposition, which participates in the electrochemical Pt dissolution reaction.

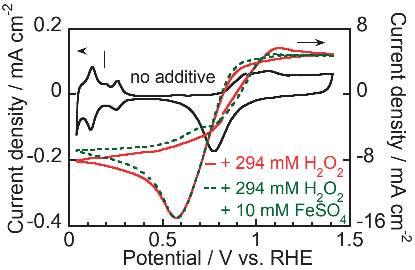


Fig. 1 Cyclic voltammograms at a Pt disk electrode in 0.5 mol dm^{-3} H_2SO_4. Sweep rate: 50 mV s^{-1}.

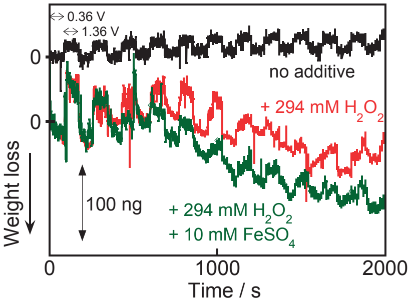


Fig. 2 Weight change in a Pt disk electrode measured by the potential step in 0.5 mol dm^{-3} H_2SO_4. Potential step range: 0.36-1.36 V vs. RHE.

Interfacial Electrochemical Processes at the Atomic Scale. Nucleation, Charge Transfer and Imaging

I. Valov[1], A. Nayak[2], T. Tsuruoka[2], T. Hasegawa[2], M. Aono[2] and R. Waser[1]
[1]*Electronic Materials, PGI-7, Research Centre Juelich, Juelich 52425, Germany*
[2]*WPI-MANA, NIMS, 1-1 Namiki, Tsukuba 305-0044, Japan*
Email: *i.valov@fz-juelich.de*

Electrochemical equilibrium and the transfer of mass and charge through interfaces at atomic scale are of a fundamental importance for the microscopic understanding of elementary physicochemical processes. At atomic dimensions, the macroscopic quantities even for single crystalline substrates show local structural defects leading to microscopic inhomogeneities of the material properties. Therefore, the atomically resolved measurements of electrochemical processes require: *a*) a high precision in detecting mass and charge flow, *b*) a stabilisation of thermodynamically meta-stable clusters of few atoms and *c*) a knowledge of the local atomic structure and topography.

In this contribution we demonstrate the ability to study electrochemical processes at vacuum/ $RbAg_4I_5$ solid electrolyte surfaces at the atomic scale[1] with an ultimate lateral, mass and charge resolution based on the atomic switch concept [2] where the new phase consists of a few to some tens of atoms (as far it can be physically defined as a phase). We show for the first time STM images of solid electrolyte at room temperature and report on the cluster dynamics and stability studied by both imaging and *I-z* spectroscopy.

The kinetics of formation of Ag nano-clusters below the STM tip was studied and analyzed in respect to the atomistic theory of nucleation accounting for the discrete character of the system for small number of atoms (N_c) constituting the critical nucleus. The nucleation time t_s (equivalent in the particular case to the switching time) is inversely proportional to the nucleation rate and is given by:

$$t_s = t_0\left(\frac{(N_c+\alpha)e\Delta\varphi}{kT}\right)$$

with $\Delta\varphi$ being the applied cathodic voltage (negative), e the elementary charge, α the transfer coefficient and t_0 the pre-exponential factor. T and k are the temperature and the Boltzmann constant, respectively.

The methodology we offer is an alternative approach for studying electrochemical reactions on a microscopic level with an ultimate lateral, mass and charge resolutions.

The possibility of extending our method to other solid and liquid based ionic conductors which are used in sensors, fuel cells, and catalysts will be highlighted.

Microcrystalline Natural Graphite–Polystyrene Composite Film – A Beneficial Electrode Interface for the Development of Electrochemical (Bio)Sensors

Vlastimil Vyskočil[1], Hana Šmejkalová[1], Zuzana Jurečková[1], Zuzana Hrochová[1],
Christian Iffelsberger[2], and Frank-Michael Matysik[2]
[1] Charles University in Prague, Faculty of Science, University Research Centre UNCE "Supramolecular Chemistry", Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Hlavova 2030/8, 12843 Prague 2, Czech Republic, e-mail: vlastimil.vyskocil@natur.cuni.cz
[2] University of Regensburg, Faculty of Chemistry and Pharmacy, Institute of Analytical Chemistry, Chemo- and Biosensors, Universitätsstraße 31, 93040 Regensburg, Germany, e-mail: frank-michael.matysik@chemie.uni-regensburg.de

A microcrystalline natural graphite–polystyrene composite film electrode (CFE) [1] represents a very promising alternative to electrode surfaces modified by carbon nanoparticles with profitable electrocatalytic properties (e.g., nanotubes or graphene). Its simple, fast, and inexpensive preparation (by covering a classical solid working electrode with a conductive composite film), simple mechanical renewal of the electrode surface (by wiping off the old film with a filter paper and forming a new one), good reproducibility of measurements, elimination of problems connected with the "electrode history", and simple chemical modification are among its main advantages [2]. Recently, it has also been shown that the CFE is a suitable transducer for the preparation of electrochemical DNA biosensors [3].

In this contribution, a complex electrochemical and microscopic characterization of the composite film will be presented, and possibilities, advantages, and limitations of this useful electrode material will be demonstrated on a number of electroanalytical methods utilizing the CFE-based (bio)sensors for the determination of various biologically active organic compounds and for the detection of the DNA damage.

The financial support provided by the Grant Agency of the Czech Republic (Project GP13-23337P), the German Academic Exchange Service (DAAD) (Project A/13/07837), and the Josef, Marie, and Zdeňka Hlávkovi Talent Foundation is gratefully acknowledged.

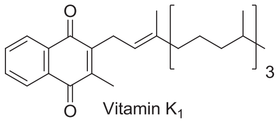
References

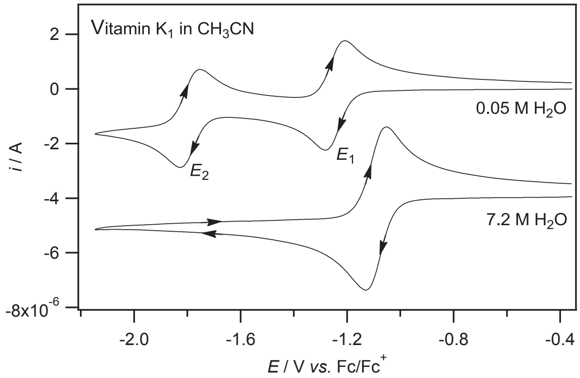
1. B. Yosypchuk, J. Barek, M. Fojta, Electroanalysis 18 (2006) 1126.
2. A.R. Khaskheli, J. Fischer, J. Barek, V. Vyskocil, Sirajuddin, M.I. Bhanger, Electrochim. Acta 101 (2013) 238.
3. V. Vyskocil, J. Barek, Procedia Chem. 6 (2012) 52.

Using the Voltammetric Behavior of Vitamin K_1 and Other Quinones to Estimate Relative Hydrogen-Bonding Strengths of Donor Compounds

Richard D. Webster, Malcolm Tessensohn, Melvyn Lee
School of Physical and Mathematical Sciences
Nanyang Technological University, 21 Nanyang Link, Singapore 637371
webster@ntu.edu.sg

Quinones are able to undergo electrochemical reduction in aprotic organic solvents such as acetonitrile and dichloromethane in two one-electron steps. The first one-electron process at E_1 produces the semiquinone anion radical; while the second one-electron reduction at E_2 leads to the dianion (E_1 and E_2 are the formal one-electron reduction potentials). As hydrogen-bond forming donors are added to the aprotic solution, both E_1 and E_2 shift to more positive potentials, but E_2 shifts much more than E_1, so that at high enough concentrations of the hydrogen-bonding donor, the two processes can merge into one two-electron chemically reversible process. It is proposed that the potential separation between E_1 and E_2 (ΔE) can be used as a measure to determine the relative strength of hydrogen-bond donors such as alcohols and other hydroxylated compounds, provided that the effects of trace water in the solvent can be minimized. Modifications can also be made to the structures of the quinones in order to enhance the hydrogen-bonding interactions with target compounds.


Vitamin K_1



Electrochemical Impedance Spectroscopy on Metallic Materials for Bipolar Plate Application in HT-PEFC

Vitali Weissbecker[a], Klaus Wippermann[a], Werner Lehnert[a,b]
[a]*Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research,*
IEK-3: Electrochemical Process Engineering, 52425 Jülich, Germany
[b]*Modeling in Electrochemical Process Engineering,*
RWTH Aachen University, Germany
v.weissbecker@fz-juelich.de, k.wippermann@fz-juelich.de,
w.lehnert@fz-juelich.de

High-temperature polymer electrolyte fuel cells (HT-PEFCs) operate in the range of 120 – 180 °C and currently employ phosphoric acid doped polybenzimidazole membranes. This in turn represents a quite aggressive environment for the components of a fuel cell. For this reason bipolar plates are presently made of graphitic composite materials. Indeed, they underlie moderate degradation due to corrosion phenomena, but otherwise they exhibit high mass and volume as well as a high effort of manufacturing. Therefore metallic materials come into play as promising candidates for bipolar plates. They provide some crucial advantages, like enhanced volumetric and gravimetric power density for stacks, increased ductility, high mechanical stability, high electronic and thermal conductivity and the capability of low-cost mass production. However, we still need further understanding of the electrochemical corrosion at the interface metal (bipolar plate) and electrolyte (phosphoric acid) at elevated temperatures.

In the present work, we focus on the investigation of the fundamental corrosion mechanism of metals in phosphoric acid that depends strongly on passive layer formation of the respective metallic material. Using an electrochemical cell, which was specially designed for these experimental requirements, we analyzed various stainless steels and Ni-based alloys by means of steady-state voltammetry and impedance spectroscopy. Additionally, ex-situ characterizations using SEM, XPS and ICP-OES were carried out in order to investigate the metallic surface and the corresponding dissolved ion species in the electrolyte. A characteristic interfacial impedance as a function of applied potential illustrates the corrosion resistance due to passivation of the surface in the domain of 0.3 – 1.2 V (vs. SHE). The corrosion resistance of Ni-based alloys in the passive region has been found to be higher in comparison to ferrous stainless steels at 130 °C. This effect is attributed to the diminished charge transfer reaction in nickel oxides and phosphates in contrast to analogous iron specimen. Negative potentials and an excess of 1.2 V, which are quite destructive for the oxide layer, induce consequently low impedance values and rising corrosion rates. Notable is the lower charge transfer resistance at the free corrosion potential, which indicates a thinner passive layer.

Electrochemical Studies of Lewis Acids for Small Molecule Activation

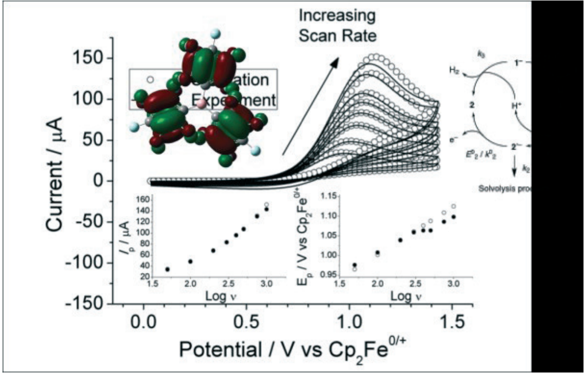
Gregory G. Wildgoose,[a] Elliot J. Lawrence,[a] Vasily S. Ogensyan,[a] David L. Hughes,[a] Andrew E. Ashley[b]

[a] Energy & Materials Laboratory
School of Chemistry
University of East Anglia
Norwich Research Park
Norwich
United Kingdom, NR4 7TJ

[b] Department of Chemistry
Imperial College, London,
South Kensington
London
United Kingdom, SW7 2AZ

G. Wildgoose@uea.ac.uk

This report summarizes our recent findings in the study of boron-based electron deficient Lewis acid complexes. The redox properties of two distinct classes of these complexes are characterized voltammetrically in non-aqueous electrolytes and the observed voltammetric behavior rationalized in terms of both the electronic and steric factors at work.[1, 2] For the first time we combine *in situ* electrochemical activation of these particular Lewis acid catalysts during small molecule activation reactions, and show that this pioneering approach significantly enhances these reactions. Detailed mechanistic studies are discussed which provides interesting insights and opens up a plethora of exciting potential applications of this pioneering approach.



References

[1] A. E. Ashley, T. J. Herrington, G. G. Wildgoose, H. Zaher, A. L. Thompson, N. H. Rees, T. Kraemer, D. O'Hare „*J. Am. Chem. Soc.*, **2011**, *133*, 14727.

[2] E. J. Lawrence, V. S. Oganesyan, G. G. Wildgoose, A. E. Ashley, *Dalton Trans.*, **2013**, *42*, 782.

Oxide Growth Kinetics during Aqueous Corrosion of Co-Cr and Ni-Cr Alloys: Potential, pH and Temperature Dependences

Mehran Behazin, Ahmed Y. Musa and Jungsook Clara Wren
Department of Chemistry, Western University
London, Ontario, Canada N6A 5B7
jcwren@uwo.ca

Cobalt-chromium alloys, such as Stellite-6, and Ni-Cr-Fe alloys, such as Inconel alloy 600, are used in many applications that require high mechanical strength and corrosion resistance. These alloys are used in some applications in nuclear power plants where they may be exposed to oxidizing water radiolysis (such as H_2O_2). Knowledge of both the uniform and localized corrosion kinetics of these materials in aggressive aqueous environments is required to assess their integrity over prolonged service lifetimes. Key to this assessment is an understanding of the relative rates of metal dissolution and oxide growth as a function of water redox environments.

We have been studying the corrosion kinetics of several transition metal alloys as a function of potential, pH, temperature and γ-radiation exposure using a combination of electrochemical measurements (include corrosion potential measurement, cyclic voltammetry, potentiostatic polarization, linear polarization and electrochemical impedance spectroscopy) and surface analyses (using SEM, Auger electron spectroscopy, x-ray photoelectron spectroscopy). The cross sections of oxide layers are examined using a focused ion beam (FIB) and SEM.

The results of these studies reveal a corrosion mechanism that is common to the different alloys. This mechanism explains the apparently different dependences of metal dissolution of the alloys on potential, pH, temperature and γ-radiation exposure. The driving force for metal oxidation is the difference between the electrochemical equilibrium potentials (ΔE_{eq}) of two half-reactions (metal oxidation coupled with water reduction). This potential difference is distributed across the surface oxide layer and the two interacting (metal/oxide and oxide/water) interfaces. The presence of oxidizing species, either chemically added or radiolytically produced, increases ΔE_{eq}. The impact of this change varies with pH and temperature. These parameters do not affect ΔE_{eq}, but they do influence the rates of key elements in the corrosion process: metal oxidation, ion migration across the oxide, metal dissolution, and oxide growth. Competition between the last two steps dictates the corrosion path that is followed.

Ultrathin Pt_xNi_{1-x} Nanowires: Tunable Composition and Electro Electrocatalytic Properties

Qiangfeng Xiao, Yang Li, Mei Cai*
General Motors Research and Development Center,
30500 Mound Road, Warren, MI 48090, USA.
Phone: 586-596-4392; Fax: 586-986-1910; Email: mei.cai@gm.com

As compared with nanoparticles, nanowires possess fewer lattice boundaries and longer segments of surface crystalline planes. Ultrathin nanowires have demonstrated higher activity and stability as electrocatalysts which is critical for long term applications in fuel cells. Although PtxNi1-x ($0\leq x\leq 1$) alloys have shown high activity as fuel cell catalyst, the obtained shapes are usually limited to nanoparticles. Here we report the synthesis of PtxNi1-x alloy ultrathin nanowires (2-3 nm in diameter) using $Cr(CO)_6$ (or (η_6-arene)$Cr(CO)_3$) as both reducing and structure directing agent. The nanowire composition can be tuned from Pt rich alloy to Ni rich alloy. The mass activity of PtxNi1-x for oxygen reduction reaction (ORR) catalysts at 0.9 V still maintain above 0.32 A/mg after 30000 cylcles which is 3.8 times that of Pt/C (0.085 A/mg).

Laser assisted photoelectrochemical etching of InGaN quantum structures

Xiaoyin Xiao, Arthur Fischer, Daniel Koleske, George Wang, Ping Lu, Richard Schneider, Jeffrey Tsao

Photoelectrochemical (PEC) etching is based on reduction or oxidation of semiconductor components by electrons or holes generated by photo excitation. For nanofabrication, PEC etching has many advantages over both wet chemical and dry plasma etching. First, PEC etching depends on light absorption and is therefore selective against materials or features which do not absorb light. Second, PEC etching can retain useful selectivity to dopants and crystal faces. In this presentation, we discuss experiments in which lasers of various wavelengths (FWHM ~2 nm) were used to PEC etch nanoscale InGaN films and quantum wires. We discuss the dependencies of etch rate on wavelength, laser power, electrode potential, and choice of solvent; and discuss the implications of these dependencies on the PEC etching mechanism.

Work at Sandia National Laboratories was supported by Sandia's Solid-State-Lighting Science Energy Frontier Research Center, funded by the U.S. Department of Energy, Office of Basic Energy Sciences. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Carbon Nanomaterials Supported $Ni(OH)_2/NiO$ Hybrid Flower Structure for Supercapacitor

Aiping Yu, Brian Kim, Victor Chabot
Assistant Professor
200 University Avenue West
Waterloo, ON, N2L 3G1, Canada
e-mail addres: aipingyu@uwaterloo.ca

In this study, flower-shaped $NiO/\alpha\text{-}Ni(OH)_2$ hybrid structures were synthesized by a solvothermal process. The microstructure, surface morphology, and surface area of the synthesized materials were characterized by XRD, SEM, and BET. It was discovered that this unique hybrid structure exhibits outstanding capacitive performance in basic electrolyte. From galvanostatic charge-discharge test, the hybrid composite itself demonstrates a solid capacitance value of 707 F/g at 2 A/g and 474 F/g at a high discharge rate of 10 A/g. In order to further improve the performance and the capacitance retention with enhanced current density, carbon nanomaterials were used as supports incorporated into the $NiO/\alpha\text{-}Ni(OH)_2$ hybrid. The effects of 4 different carbon nanomaterials supports, including carbon black, carbon nanotubes, and graphene, were thoroughly investigated, and specifically the addition of single-walled carbon nanotubes to the composite significantly enhanced the performance to 810 F/g at a high current discharge of 10 A/g. Moreover, this carbon supported hybrid composite exhibits an impressive specific power density of 7200 W/kg and a steady energy density of 21 Wh/kg.

Electrochemical Heterogeneity in “Ideally Behaved” Redox Self-Assembled Monolayers on Gold

Hua-Zhong (Hogan) Yu
Simon Fraser University, Department of Chemistry
8888 University Drive, Burnaby, BC V5A1S6, Canada
e-mail address: hogan_yu@sfu.ca

Redox-active self-assembled monolayers (SAMs) on gold are excellent model systems for the study of long-range electron transfer process at electrolyte-electrode interfaces, particularly the distance and reorganization dependences. Ferrocene-terminated self-assembled monolayers (Fc-SAMs) have been extensively studied in the past because of their easy preparation, good reproducibility, and well-defined electrochemistry. The redox behavior of Fc-SAMs is in fact typically “non-ideal”, and influenced by the microenvironment, e.g., double layer and ion-pairing effects that are associated with both monolayer structure and the electrolyte; we demonstrate herein that Fc-SAMs are ideal probes to study the structure, redox property, and intermolecular interactions in both single-component and mixed monolayers on gold.

In this work, we first examined the redox behavior of single component 11-ferrocenyl-1- undecanethiolate SAMs on gold (FcC11S-Au), and discovered that the two distinct pairs of redox peaks are corresponding to rather moderate differences in the packing densities of the two structural domains. Upon adding small amount of nitrobenzene or octanol to the aqueous electrolyte, the two peaks responded differently in terms of shape change and potential shift. On the basis of the Frumkin isotherm, we have fitted the intermolecular interaction parameters in the two different structural domains of the monolayers, which can be individually modulated by either changing the composition of the monolayer or adding organic solvents to the aqueous electrolyte.

With the above success of understanding intermolecular interactions in Fc-SAMs, we went ahead to compare “ideally behaved” redox-active self-assembled monolayers on gold prepared from post-assembly exchange and co-adsorption processes, respectively. The ideal binary FcC11S-/C11S-Au SAMs from the two methods have been carefully compared by fitting the CVs in consideration of the intermolecular interactions. The different distributions of the redox centers in the binary SAMs, as indicated by the distinct formal potentials and intermolecular repulsions, were explained in terms of their kinetically vs. thermodynamically controlled formation processes.

Research and Development of Non-Pt Electrocatalysts for Proton Exchange Membrane Fuel Cells

Huaming Zhang , Hexiang Zhong
Division of Energy Storage, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences
No.457 Zhongshan Road, Dalian 116023, China
Email:zhanghm@dicp.ac.cn

Due to its advantages such as high efficiency and environment friendly, proton exchange membrane fuel cells (PEMFC) have been recognized as a potential energy generator[1]. Platinum (Pt) supported on carbon has been regarded as the most active catalyst for oxygen reduction reaction (ORR) in PEMFCs[2]. However, the high cost and very limited resource of Pt hamper the widespread applications of the Pt/C catalyst-based fuel cells. Therefore, there is an urgent requirement for exploring alternative low-cost electrocatalysts with high activity and stability.

Herein, the research progresses of non-platinum electrocatalysts including chalcogenides and nitrogen-doped carbon materials for PEMFC capable of combining high activity and stability with low cost are presented. The ORR catalytic activity and catalytic mechanism of the catalysts in PEMFC have been investigated. The Ru-based chalcogenide and Ir-based catalysts were synthesized by novel method using cheap and readily available starting materials of $RuCl_3$ and Na_2SeO_3. The preparation method can effectively control the particle size and prevent the agglomeration of nanoparticles, which contributes to the high ORR activity of the Ru-based and Ir-based catalyst. The nitrogen-doped carbon catalysts derived from resorsinol formaldehyde, melamine resins and conducting polymers by different synthesis methods have been investigated. The PANI-based catalyst achieves the best performance. It displays high catalytic activity with the ORR onset potential of 0.900 V in electrochemical measurements and the maximum power density about 456 mW cm^{-2} in single cells tests, as well as superior poison tolerances and stability in acid medium. Moreover, it presents superior activity, and stability than 20% Pt/C in alkaline electrolyte. The non-platinum catalysts bring us promising alternatives of Pt-based precious catalysts, which makes the PEMFC an efficient technology.

Acknowledgments

The authors acknowledge financial support from the National Program on Key Basic Research Project (973 Program, 2012CB215500).

Documents

[1] Handbook of Fuel Cells---Fundamentals Technology and Applications; vol. 3–4, Part 3.
[2] Borup, R.; Meyers,et al., Chem. Rev. 2007, 107 (10), 3904-3951.

Quantum chemical study on electrochemical catalytic oxidation of p-amino phenol at p-amino phenol modified graphite electrode with diazo-reaction

Yongchun Zhu, Qingxiao Jiang, Ying Gao, Amin Bao, Nan Xiao, Shigang Xin
College of hemistry and Life sciences, Shenyang Normal University
253 Huanghe street anggu District, Shenyang Liaoning, P.R. of China
e-mail address:yongchunzhu@126.com

The graphite powder surface was chemically modified with p-amino phenol by diazo-reaction, and used to make a carbon paste electrode. The modified electrode shows an electrochemical catalytic behavior for the electrochemical oxidation of p-amino phenol with negative shift of oxidation potential about 90 mV and increase in oxidation peak current about 75% compared with the carbon paste electrode without the modification.

In order to understand the catalytic behavior, quantum chemistry calculation was performed with PM6 in MOPAC2012 software based on the molecular models of a piece of graphene including 38 carbon atoms as the surface of graphite powder, and p-amino phenol and its diazo-reaction product in vacuum conditions. The oxidation process directly related to the ionization potential of a molecule because of the removing one electron from the highest occupied molecular orbital (HOMO). The calculated ionization potentials were obtained as 7.625, 8.211, 8.286,7.615 and 7.650 eV for carbon 38, p-amino-phenol, modified carbon 38 with p-amino phenol, modified carbon 38 with free p-amino phenol, and carbon 38 with free p-amino phenol, respectively. The π molecular HOMO is mainly composed of p_z carbon atomic orbitals from grapheme carbon 38. It seems to have nothing to do with p-amino phenol, which needs more energy to remove one electron from the molecules. But analyzing the next HOMO orbital of modified carbon 38 with free p-amino phenol, and carbon 38 with free p-amino phenol, it was found that the next HOMOs were composed of carbon p_z atomic orbitals from carbon 38 carbon p_z atomic orbitals from carbon 38, carbon p_z , p_x, p_z from carbon, nitrogen and oxygen of the diazo product and free p-amino phenol. The difference of the first HOMO and the next HOMO was 0.392 eV for modified carbon 38 with free p-amino phenol and 0.46 eV for carbon 38 with free p-amino phenol.

The calculation results mean that positive potential draws out one electron from electrode material of graphite powder and then induces the p-amino phenol gives out one electron to the first HOMO which becomes LUMO, and shows the electrochemical catalytic behavior, which is accord well with the experimental results.

Micro/Nano- Approaches for Biosensing Applications

Zhigang Zhu [1, 2*], Cheng Chen[1], Andrew J. Flewitt[2], Francis Moussy[3]
1. *School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai 201209, China*
2. *Electrical Engineering Division, Department of Engineering, University of Cambridge, J J Thomson Avenue, Cambridge, CB3 0FA, UK*
3. *Brunel Institute for Bioengineering, Brunel University, Uxbridge, UB8 3PH, UK*

Correspondence: zgzhu@sspu.edu.cn

Biosensors are a type of bio-molecular probe that measure the concentration of biological molecules by transducing a biochemical interaction into a quantifiable electrical signal. There is intensive interest in the use of micro and nano approach for such applications, and this talk is focused on implantable glucose biosensor, including Pt coil-type implantable sensor, carbon nanotube (CNT) fiber based enzymatic sensor and CNT/Ni nanocomposite based non-enzymatic sensor.

To improve the life-time of glucose sensor implanted underneath the skin, a new type of Pt coil electrode was introduced, which is able to immobilize much more GOD than traditional needle type electrode. The selection of semi-permeable membrane is critical for the sensor linearity. The sensors could be survived for 4 weeks during in-vivo test, and histology revealed that the fibrous capsules surrounding hydrogel-coated sensors were thinner than before.

A novel brush-like electrode based on carbon nanotube (CNT) fiber has been designed for electrochemical biosensor applications and its efficacy as an enzymatic glucose biosensor was demonstrated. The electrode end-tip of the CNT fiber was freeze-fractured to obtain a unique brush-like nano-structure resembling a scale-down electrical ‘flex’. The sensitivities, linear detection range and linearity for detecting glucose for the miniature CNT fiber electrode were better than that reported for Pt-Ir coil electrode. In addition, gold coating of the CNT fiber electrode resulted in extending the glucose detection limit to 25 μM.

A highly sensitive nonenzymatic amperometric glucose sensor was fabricated by using Ni nanoparticles homogeneous dispersed within and on the top of a vertically aligned CNT forest. The CNT/Ni nanocomposite sensor exhibited a great enhancement of anodic peak current after adding 5mM glucose in alkaline solution. The sensor can also be applied to the quantification of glucose content with a linear range covering from 5 μM to 7 mM, a high sensitivity of 1433 μA mM^{-1} cm^{-2}, and a low detection limit of 2 μM.

Interfacial functionalization of nanostructured metal nanoparticles: from changes in spectrochemical identity to enhancement of electrocatalytic properties

Sylwia Zoladek, Iwona A. Rutkowska, Pawel J. Kulesza
Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland
** pkulesza@chem.uw.edu.pl*

Of particular interest to the preparation of advanced materials is synthesis and characterization of metal (e.g. Au, Ag, Cu and such noble metal as Pt or PtRu) nanoparticles, their stabilization (e.g. through self-assembly), as well as organization into two-dimensional arrays and controlled fabrication (e.g. through the sequential attraction) into three-dimensional network films. They can form nanosized materials with well-defined composition, structure and thickness. The interfaces can be also highly functionalized, and they can exhibit specific catalytic or unique electronic, plasmonic, charge storage, optical and sensing properties. We explore here the ability of inorganic structures to stabilize and derivatize metal and carbon nanostructures. Among inorganic systems, polyoxometallates of molybdenum and tungsten are attractive since they can not only adsorb irreversibly on solid surfaces but also exhibit reversible stepwise multielectron transfer reactions. The concept of the layer-by-layer formation of hybrid (organic-inorganic) assemblies composed of anionic polyoxometallate-protected carbon nanotubes (or metal nanoparticles) and ultra-thin films of positively charged conducting polymers (e.g. such as polyaniline or PEDOT) will be described and discussed here. The resulting novel composite materials have been fabricated as thin or moderately thick (μm level) films on electrode surfaces. As evidenced from STM and scanning electron microscopy, their morphology is still granular but the structure is fairly dense. Further, they are characterized by fast dynamics of charge propagation. Obviously, this research is of importance to the construction of effectively operating charge storage devices (capacitors), charge mediators (e.g. in bioelectrochemistry), molecular electronic systems and electrocatalysis. In the latter case, polyoxometallates can also be applied to stabilize and link Pt-Ru, Pt-Sn and various alloyed Pt-based nanoparticles. It is apparent from diagnostic cyclic voltammetric, rotating disk voltammetric and chronoamperometric measurements that such systems exhibit attractive properties towards electroreduction of oxygen or oxidation of alcohols (ethanol, methanol). Here, it is possible that addition of polytungstate or molybdate clusters to ruthenium or tin hydroxo species at the catalytic interface results in activating effect on dispersed platinum particles. An alternate explanation may involve a possibility of electronic effects and/or different morphologies of the catalytic films in the presence and absence of polyoxometallate.

Development of Biofilm-Supported Hybrid Electrocatalytic Materials for Biosensing and Bioenergetics

W. Lotowska[1], E. Szaniawska[1], E. Seta[1], M. Gierwatowska[1], B. Kowalewska[1], S. Zoladek[1], I.A. Rutkowska[1], A. Raczkowska[2], K. Brzostek[2], P.J Kulesza[1]
[1]Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland
[2] Faculty of Biology, University of Warsaw, Miecznikowa 1, PL-02-093 Warsaw, Poland
pkulesza@chem.uw.edu.pl

We explore unique properties of biofilms, i.e. polymeric aggregates of microorganisms, in which cells adhere to each other on the electrode surfaces. Such systems are characterized by extracellular electron transfers involving c-type cytochromes (heme-containing proteins). Biofilms grown on inert carbon electrode substrates tend to exhibit electrocatalytic properties towards oxygen and hydrogen peroxide reductions in neutral media. The processes have been found to be further enhanced by introduction of multi-walled carbon nanotubes (MCNTs) that are modified with ultra-thin layers of organic (e.g. 4-(pyrrole-l-yl) benzoic acid. We expect here attractive electrostatic interactions between carboxyl-group containing anionic adsorbates and positively charged domains of the biofilm with c-type cytochrome enzymatic sites. Coexistence of the above components leads to synergistic effect that is evident from positive shift of the oxygen reduction voltammetric potentials and significant increase of voltammetric currents. Most likely, the reduction of oxygen has been initiated at the molecular (e.g. intentionally added cobalt porphyrin redox centers), whereas the undesirable hydrogen peroxide intermediate are further decomposed at the cytochrome sites.

Fabrication of the biofilm based matrices for anodic reactions has also been considered. To facilitate electron transfers between the electrode surface and the redox protein centers, the concept of codeposition of multi-walled carbon nanotubes within the bioelectrocatalytic film has also been pursued here. First, carbon nanotubes are modified with ultra-thin layers of tetrathiafulvalene (TTF) or poly(dimethyldiallylammonium chloride) (PDDA) mediators. Their presence is expected to facilitate flow of electrons from the enzyme (e.g. glucose oxidase) active sites through biofilm to the electrode surface. Combination of intentionally derivatized carbon nanotubes with biofilm matrtices and the appropriate enzymes seems to produce biocatalytic systems capable of effective oxidation and sensing of glucose or ethanol in the neutral buffered solution.

Development of Nanoprobe for Localized Quantitative Detection of Mn^{2+} Produced at Battery Material

Laurence Danis, Michael E. Snowden, Janine Mauzeroll*
Chemistry Department, McGill University.
3420 Rue University, Pulp and Paper- 109C Montreal, Quebec, Canada, H3A 2A7
Laurence.danis@mail.mcgill.ca

The spinel $LiMn_2O_4$ is one of the most promising cathode materials for lithium batteries. It exhibits very good electrochemical performance at room temperature. However, its capacity fades with charge-discharge cycling or storage. This capacity fading is due to numerous factors such as the Jahn-Teller distortion and the dissolution of Mn^{2+} into the electrolyte.[1] Although the exact mechanism is still unclear, most research groups agree that dissolution of Mn^{2+} is the leading factor for the decreased capacity. [2] Our ongoing research efforts focus on spatially resolved, quantitative detection of Mn^{2+} produced at battery materials, using a platinum-mercury nanoelectrode under anaerobic conditions, combined with shear-force constant-distance scanning electrochemical microscopy (SECM). Our probe scanner also allows the local measurement of the topography and the reactivity of the battery material during charge-discharge reactions with high resolution. The work presented here directly relates to the development and characterization of shear force Hg/Pt hemispherical nanoelectrodes. The production of this type of electrochemical probe is performed by electrodeposition from a mercuric ion solution on a Pt/quartz laser-pulled concentric disk nanoelectrode. [3] These standard nanoelectrode tips exhibit very stable shear force behavior. It has been reported that amalgam electrodes can be used to perform the quantitative analysis of Mn^{2+} due to extension of the potential window to more negative potentials. [4] An enhanced sensitivity of the substrate generation-tip collection (SG-TC) results has also been reported. The enhancement in sensitivity of this SECM mode and positioning capability of our system will give us a competitive advantage in the mapping of Mn^{2+} hot spots at battery materials as the reaction is ongoing with high resolution.

[1] A. Du Pasquier, A. Blyr, P. Courjal, D. Larcher, G. Amatucci, B. Gérand, J.M. Tarascon, Journal of the Electrochemical Society, 146 (1999) 428-436.
[2] Y. Kim, J. Lim, S. Kang, International Journal of Quantum Chemistry, 113 (2013) 148-154.
[3] J. Mauzeroll, E.A. Hueske, A.J. Bard, Analytical Chemistry, 75 (2003) 3880-3889.
[4] D. Rudolph, S. Neuhuber, C. Kranz, M. Taillefert, B. Mizaikoff, Analyst, 129 (2004) 443-448.

s1-001

Impedance Transfer Function Designed to Simulate a Capacitive Behavior as a Function of Solute Concentration Evaluated for DNA-Au and DNA-Pt Interfaces.

L.M. Bravo-Anaya[1], J.F.A. Soltero[1], E. R. Macías[1], J. Gómez Gómez[1], V.V. Fernández Escamilla[2], M.A. Carreón Alvarez[3], E.R. Larios-Durán[1*]
[1] Universidad de Guadalajara. Departamento de Ingeniería Química y [2]Química, Blvd. M. García Barragán #1451, C. P. 44430, Guadalajara, Jalisco, Mex.
[2] Universidad de Guadalajara, Departamento de Ciencias Tecnológicas, Av. Universidad # 1115, C.P. 47810, Ocotlán, Jalisco, Mex.
[3] Universidad de Guadalajara, Carretera Guadalajara-Ameca Km. 45.5, C.P. 46600, Ameca, Jalisco, Mex.
**roxana.larios@red.cucei.udg.mx*

Impedance transfer function development is essential for a clear understanding of the faradaic or the non-faradaic response of processes taking place at the electrode-electrolyte interface. However, although a great amount of processes have been profoundly studied during several years in electrochemistry, a relation between impedance data and solute concentration was not proposed in the past. On the other hand, the interactions of biological biomacromolecules with surfaces, which are very important in nature and in biotechnology, depend strongly on the concentration of these molecules. DNA, known as the most important biomolecule, has been studied in the field of linear polymers in solution and is characterized by having three typical regimes, bounded by two critical parameters sensible to DNA conformation, i.e. the overlap (C^*) and the entanglement (C_e) concentration. A transfer function able to simulate the impedance behavior obtained by an adsorption processs at the electrode surface and evaluated as a function of solute concentration at each characteristic regime is proposed in this work. The behaviour of the solution resistance (R_s) and the characteristic time-constant of the process (τ_c) can be expressed in terms of a power law with specific values at each regime. Since EIS measurements are carried out at OCP, it is possible then to generalize a transfer function through the impedance function for an ideally polarizable electrode expressed in terms of a CPE [1] and through the scaling of R_s and τ_c parameters [2]. Au-calf thymus DNA and Pt-calf thymus DNA interfaces were used to evaluate this transfer function. Calf-thymus DNA (13 kpb) was studied in a range from 0.01 to 3.0 mg mL^{-1} at a constant pH of 7.3 and at the temperatures of 10, 20, 30 and 40 ºC for platinum electrodes and 25, 30 and 35 ºC for gold electrodes. The transfer function allows predicting the impedance behavior, the electrical parameters involved in the process and the characteristic time-constant for every concentration within its characteristic regime at OCP setup. Therefore, it also allows analyzing the double-layer charging behavior as a function of concentration.

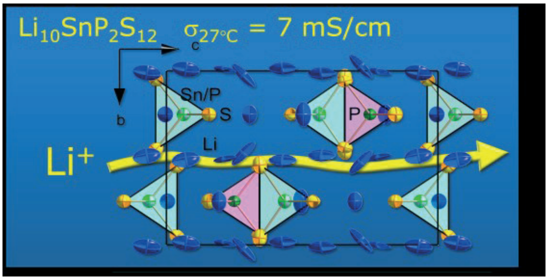
s1-002

$Li_{10}SnP_2S_{12}$: An Affordable Lithium Superionic Conductor

Philipp Bron,[†] Bernhard Roling,[†] Stefanie Dehnen,[†]
Sebastian Johansson,[‡] Jörn Schmedt auf der Günne,[‡] Klaus Zick[⊥]
[†]*Department of Chemistry, University of Marburg, 35032 Marburg, Germany*
[‡]*Department of Chemistry/Biology, University of Siegen, 57068 Siegen, Germany*
[⊥]*Bruker Biospin GmbH, 76287 Rheinstetten, Germany*
bron@chemie.uni-marburg.de

Until now, the integration of solid electrolytes in batteries was strongly hindered by the poor ionic conductivity of most solid lithium ion conductors. In 2011, Kanno et al. reported the synthesis of Li10GeP2S12.[1] With a conductivity of 12 mS/cm at 27 °C it exhibits the highest lithium ion conductivity known to date. But the major drawbacks for its application in batteries are the scarce deposits and high cost of germanium.

We synthesized and characterized the thiostannate analogue $Li_{10}SnP_2S_{12}$, which exhibits a very high grain conductivity of 7 $mS{\cdot}cm^{-1}$ at 27 °C.[2] The replacement of Ge by Sn should reduce the raw material cost by a factor of about 3 and the total conductivity of 4 mS/cm still exceeds the lithium ion conductivity of the carbonate-based liquid electrolytes, when the lithium trans-ference numbers are taken into account.



[1] Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; Mitsui, A. *Nat. Mater.* **2011**, *10*, 682.

[2] Bron, P.; Johansson, S.; Zick, K.; Schmedt auf der Günne, J.; Roling, B.; Dehnen, S. *Chem. Mater.* **2012**, *24*, 2211.

s1-003

An Investigation of the pH Dependent Barrier Properties of Scaffolded Vesicles

S. Conlon, R. Seenath, J. Lipkowski
Department of Chemistry, University of Guelph
50 Stone Rd E. Guelph, ON, N1G 2W1
sconlon@uoguelph.ca

Nutraceutical carriers rely on multiple features in order to function properly upon ingestion. These features include controlled permeability and biocompatibility. A recently proposed nutraceutical carrier composed of a phospholipid bilayer physisorbed to a hydrogel surface. This nutraceutical carrier, known as the scaffolded vesicle, has been designed to include these important features and current investigations are now focusing on triggered release mechanisms. The scaffolded vesicle is composed of a lipid membrane encapsulated hydrogel. The lipid membrane offers a relatively impermeable barrier, as well as the possibility of tuning the pH dependent permeability of the lipid membrane.

The fluorescent properties of the terbium/2,6-pyridinedicarboxylic acid complex is used to monitor the temporal stability of the scaffolded vesicle. The hydrogel beads are loaded with Tb^{3+}, and the leakage over time is determined through the intensity of fluorescence in the exterior supernatant. The current project is focused on the pH sensitivity of the lipid composition of the membrane. Preliminary results have shown that the pH stability of a scaffolded vesicle is determined by the pK_a value of the pH triggers incorporated into the membrane. By altering both the composition and the pH trigger species, a scaffolded vesicle can be designed to release its contents at specific pH environments in the gastric intestinal tract.

s1-004

Study of the Electrochemical oxidation of Dissolved Carbon monoxide in Acidic and Alkaline electrolytes by Using Au-RDE and Fabricated Au-Microelectrode

Trav Cheng-Yi Huang, Andrew S.Lin*
Department of Chemical and Materials Engineering ,Chang Gung University,
Taoyuan ,Taiwan
E-mail:andrew@mail.cgu.edu.tw

Microelectrode is defined as having at least one dimension of an electrode in the micrometers , and the importance of these electrodes is (i) very little current passes; (ii) small size; (iii) there is a transition from linear to spherical diffusion at increasing time of measurement.

In this study, gold(Au) was used to study the electrochemical oxidation of carbon monoxide(CO) in acidic or alkaline electrolytes. The electrochemical oxidation of dissolved carbon monoxide(CO) on Au-RDE is mainly diffusion-controlled process at the potential greater than 0.6V(vs. RHE) and 0V(vs. RHE) in acidic and alkaline electrolytes, respectively. Fabricated Au-microelectrode was used to study the rates of mass transfer of the dissolved carbon monoxide(CO) electrocatalysis in acidic and alkaline system. Using Au-microelectrode high limit currents without rotation can achieved.

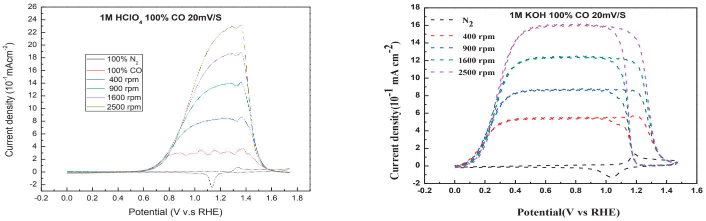


Figure.1 Au-RDE in 1M $HClO_4$ (left) and 1M KOH (right) saturated with 10^{-3}M CO at rotating speeds of 400, 900, 1600 and 2500 rpm.

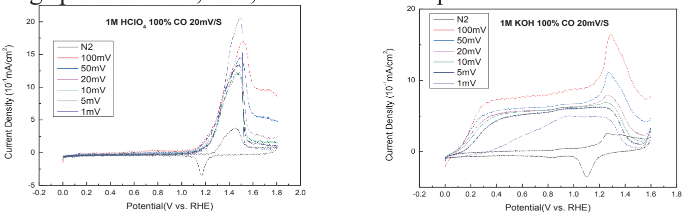


Figure.2 Fabricated Au-Microelectrode in 1M $HClO_4$ (left) and 1M KOH (right) saturated with 10^{-3}M CO at different scan rates of 1, 5, 10, 20, 50and 100 mV/s.

s1-005

Carbon Nanotubes Modified with Anticancer Drugs and Their Interactions with Model Membranes.

Dorota Matyszewska[1], Jan F. Biernat[2], Renata Bilewicz[1]
[1]*Faculty of Chemistry, University of Warsaw*
ul. Pasteura 1, 02093 Warsaw, Poland
[2]*Chemical Faculty, Gdansk University of Technology, ul. Narutowicza 11/12,*
80233 Gdansk, Poland
dorota.matyszewska@chem.uw.edu.pl

Carbon nanotubes are often treated as an alternative to common drug delivery systems such as liposomes or micelles [1]. There are many examples of their applications in the delivery of anticancer drugs [2]. The interactions of single-walled carbon nanotubes (SWCNTs) with model membranes prepared by means of Langmuir technique were investigated. Basing on our previous studies, the model membranes were composed of a thiolipid, 1,2-dipalmitoyl-*sn*-glycero-3-phosphothioethanol (DPPTE) [3]. The main advantage of such composition of model membranes is the fact that due to the presence of the thiol group, DPPTE monolayers can be transferred onto a solid support by means of both Langmuir-Blodgett technique and self-assembly [4]. Electrochemical methods including chronocoulometry along with AFM studies allowed us to compare the organization and structure of supported DPPTE model membranes depending on the method of transfer [3].

Single-walled carbon nanotubes were used as potential drug delivery systems and were modified with an anticancer drugs doxorubicin (DOx) and daunomycin (DAU). Stable adducts of both drugs were obtained by forming hydrazone with the nanotubes [5]. The drugs were attached either at the ends or sides of the nanotubes. Initial characterization of the interaction of the two types of adducts with model thiolipid membranes was performed at the air-water interface by means of Langmuir technique. The mixed layers of modified nanotubes and thiolipid were formed. In the next part of the studies the layers containing SWCNTs-drug adducts were transferred by means of Langmuir-Blodgett technique to solid support to perform microscopic and electrochemical studies. Cyclic voltammetry was used to verify the efficiency of the nanotube modification with doxorubicin and daunorubicin. It has been confirmed that the drugs were not only adsorbed but also covalently bound to the nanocarriers. Additionally, the two types of carbon nanotubes modification with anticancer drugs (end and side) were compared basing on the electrochemical signal obtained from the electroactive drugs.

s1-006

Electrochemical Investigation of Functionalized Gold Nanoparticles onto Electrode Surface

Sana Sabahat*[a,b,c], Naveed Kausar Janjua [a], Zareen Akhter [a]
[a]*Department of Chemistry, Quaid-i-Azam University Islamabad, Pakistan.*
[b]*Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD UK.*
[c]*COMSATS Institute of Information Technology Islamabad, Pakistan.*
**E.mail: s.sabahat@comsats.edu.pk*

Electrochemistry has been employed for the quantification of functionalized gold nanoparticles in nanoscale domain. Ferrocene being a potential anti-cancer agent, is active by causing oxidational damage to DNA. Unfortunately, it is practically insoluble in water, which makes its delivery to the site of activity very difficult within a biological environment. Here we demonstrate that thiol-modified ferrocene (Fc-SH) is readily solubilised when attached to highly water-soluble mercaptoalkyl-oligoethylenegylcol (PEG) gold nanoparticles (AuNPs). Importantly, it retains its redox activity under these conditions as observed by electrochemical studies. The functionalized gold nanoparticles have been successfully quantified by employing electrochemical techniques. Cyclic voltammetry has extensively been used for monitoring the adsorptive and diffusion studies of functionalized gold nanoparticles.

s1-007

Electrochemistry of tri-manganese substituted Keggin-ions

Jochen Friedl [a,b], Rami Al-Oweini [c], Max Herpich [a,b], Ulrich Kortz [c], Ulrich Stimming [a,b,d]
[a] TUM CREATE, 1 CREATE Way, CREATE Tower, Singapore 138602, Singapore
[b] Department of Physics E19, Technische Universität München, James-Franck Str. 1, 85748 Garching, Germany
[c] Jacobs University, School of Engineering and Science, 28725 Bremen, Germany
[d] Institute for Advanced Study (IAS) of the Technische Universität München, Lichtenbergstr. 2a, 85748 Garching, Germany
Ulrich.Stimming@tum-create.edu.sg

Polyoxometalates (POMs) are discrete metal-oxo anions of early transition-metals in high oxidation states representing a unique class of inorganic cage complexes [1]. Keggin-type POMs are of special versatility as they can release one or more W-O units and thereby form lacunary derivatives; these lacunaries can be filled again by transition metals. The inserted metals are redox-active and add their characteristics to the already rich redox-activity of the Keggin-ion.

We report the electrochemistry of the tri-Manganese substituted Keggin-ions $[Mn^{II}_3(OH)_3(H_2O)_3(A\text{-}\alpha\text{-}SiW_9O_{34})]^{7-}$ ($Mn^{II}_3SiW_9$) and $[Mn^{III}_3(OH)_3(H_2O)_3(A\text{-}\alpha\text{-}SiW_9O_{34})]^{4-}$ ($Mn^{III}_3SiW_9$) in aqueous solution. To showcase the changes that are evoked by insertion of Mn we also present the parent heteropolyacid $[A\text{-}\alpha\text{-}SiW_{12}O_{40}]^{4-}$, mono- and tri-lacunary derivatives and the mono-Mn substituted POM.

Although $Mn^{II}_3SiW_9$ and $Mn^{III}_3SiW_9$ represent the same molecule in different oxidation states, their redox properties are quite different. We attribute this to a ligand exchange which takes place when the Mn redox-centers are in oxidation state Mn^{II}. Three bound water-molecules are replaced by molecules of the supporting electrolyte. To our knowledge this is the first report that ligand exchange leads to a substantially modified redox-behavior for POMs.

Investigating the electron transfer kinetics we found them to be fairly facile, with an electron transfer constant on the order of 10^{-2} cm s^{-1}. Fast redox-kinetics were assigned to small solvent reorganization energy due to the large inorganic framework of the molecule. Furthermore, we investigated the adsorption-behavior of the POMs on graphite with Atomic Force Microscopy which is in accordance with predictions from the Born solvation model.

[1] U. Kortz, A. Müller, J. van Slageren, J. Schnack, N.S. Dalal, M. Dressel, Coord. Chem. Rev. 253 (2009) 2315.

s1-008

Charge Transfer through Metal Nanoparticle Thin Layers: Effect of Particle Size, Ligand Length, and Anchoring Element

Georgeta C. Lica[1], Ying Li[1], Yuan Gao[1], Yangwei Liu[1], Thomas C. Allison[2], and
YuYe J. Tong[1],
[1]Department of Chemistry, Georgetown University
37th & O Streets, NW, Washington DC 20057, USA; [2]Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8320, Gaithersburg, MD, 20899-8320, USA
yyt@georgetown.eu

Understanding mechanistically charge transfer/transport (CT) through metal nanoparticle (NP) assemblies is of fundamental importance for the majority if not all metal-NP-based potential applications in nano-electronics, nano-optics, and (bio)nano-sensing[1]. In this presentation, we will discuss electrochemical studies of CT through alkylchalcogenolate (S-, Se-, and Te-) protected Au and Ag NP thin layers (~300 nm thick) formed by drop-casting the NP solutions onto a glassy carbon (GC) electrode as schematically illustrated in Fig.1a. Fig.1b shows the cyclic voltammograms (CV) of a 1.7nm Au NP thin film (black), together with those of the probing redox species $Fe(CN)_6^{3-}$ (red) and $SiW_{12}O_{40}^{4-}$ (blue) on bare GC electrode whose CV is the dashed one. The Nicholson method[2] in which the peak separation of a redox pair ΔE_p for quasi-reversible systems as a function of potential scan rate was used to extract the CT kinetic constants. The obtained results show clearly that the CT kinetics can be controlled by the NP size, the anchoring element (S, Se, or Te), the alkyl chain length (C8, C10, and C12), and the metal element (Au vs Ag). The majority of the results are consistent with the theoretical calculations.

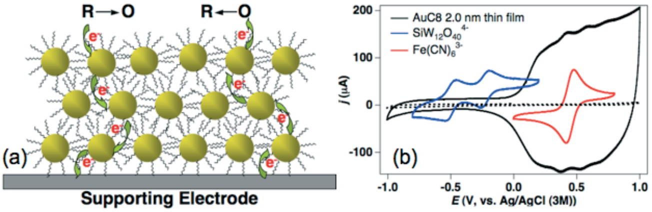


Figure 1. A. A cartoon representation of an ideal Au NP thin film for redox CT. **B.** The CV (black) of a GC-supported 1.7 nm Au NP thin film in a 0.1 M $LiClO_4$ aqueous electrolyte. Quantized charging /discharging peaks are visible in the positive potential region. The insets are the CVs of probing redox species, 1 mM $Fe(CN)_6^{3-}$ (red) and 0.1 mM $SiW_{12}O_{40}^{4-}$ (blue, x 4 current scale was used) respectively, on bare GC electrode whose background is presented by the dashed curve.

1. *a*. Pelaz, B. et al. *ACS Nano* **2012**, *6*, 8468; *b*. Shipway, A. N. et al. *ChemPhysChem* **2000**, *1*, 18.
2. Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

s2-001

Carbazole Based Star-Shaped Oligomers for Optoelectronics Applications.

Przemyslaw Data[a,b], Przemyslaw Ledwon[a], Pawel Zassowski[a], Mieczyslaw Lapkowski[a,b], Alina Brzeczek[c], Krzysztof Walczak[c]
[a] *Silesian University of Technology, Faculty of Chemistry, Department of Physical Chemistry and Technology of Polymers, 44-100 Gliwice, Strzody 9, Poland*
[b] *Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 41-819 Zabrze, Curie-Sklodowskiej 34, Poland*
[c] *Silesian University of Technology, Faculty of Chemistry, Department of Organic Chemistry, Bioorganic Chemistry and Biotechnology, 44-100 Gliwice, Krzywoustego 4, Poland*
przemyslaw.data@polsl.pl

Carbazole based compounds are very promising group of π-conjugated organic materials for applications in optoelectronics and photovoltaics. In recent years it is observed increased number of papers focused on synthesis and properties of carbazole based materials. The star-shaped structure of the π-conjugated systems is one of the strategies used in new organic semiconductors. The development of these compounds results from the fact that these compounds present different properties than linear analogues. Star-shaped compounds can be used as active materials or as a starting monomer for highly branched conjugated polymers.

We synthesized symmetric, soluble star-shaped molecules based on carbazoles (figure 1). The electrochemical and spectral studies are presented. These compounds are electrochemically and fluorescently active. These studies were supported by DFT calculations. Studied carbazole derivatives were used to fabrication of organic light emitting diodes. Presented star-shaped oligomers were also used as precursors of promising branched π-conjugated polymers.

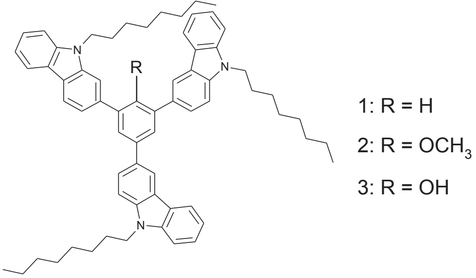


Figure 1 Structures of studied star-shaped, carbazole based molecules.

Acknowledgements. This work was supported by National Science Centre, Project No. 2012/05/B/ST5/00745.

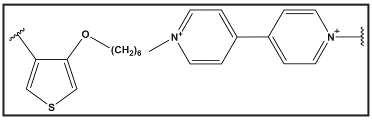
s2-002

Polythiophene derivative with pendant viologen side group: *In situ* ESR/UV-Vis-NIR spectroelectrochemical study

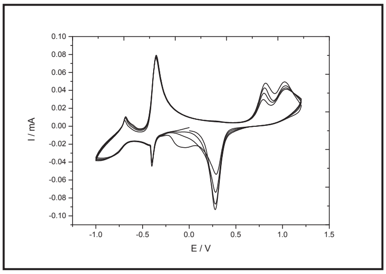
Bhushan Gadgil, Carita Kvarnström
Turku University Centre for Materials and Surfaces (Matsurf), Laboratory of Materials Chemistry and Chemical Analysis, University of Turku,
Vatselankatu 2, FI-20014 Turku, Finland
bhushan.gadgil@utu.fi

Recently, considerable research has been developed in modifying the electronic properties of conducting polymers mainly by attaching specific functional groups to the polymeric chain, so called third generation of polymers. Viologen is such a functional group which can give additional redox properties to the polymeric backbone, besides the electrical conductivity. 1-[6-[(4-methyl-3- thienyl) oxy] hexyl]-4,4´-bipyridium hexafluorophosphate (Th-V) was synthesized and electropolymerized to form a viologen bearing polythiophene (PTh-V) film on an electrode surface. The resulting polymer shows electrochemical activity from both viologen and polythiophene moieties. The redox behavior of *n* and *p* doped PTh-V was studied by *in situ* spectroelectrochemical study by means of simultaneous recording of electron spin resonance–UV–vis–near infrared spectra (ESR/UV–Vis–NIR) with the aim of obtaining details about the nature of charge carriers involved within the polymer. The polymer film shows enhancement of electrochromic contrast due to incorporation of pendant viologen group with coloring characteristics both of the viologen and the polythiophene backbone.

Figures



1. Structure of the monomer Th-V



2. Redox response of polymer PTh-V

References

1. B. Gadgil et al., Electrochim. Acta 97, (2013), 378– 385.
2. H.C. Ko et.al., Adv. Funct. Mater. 15, (2005), 905-909.

s2-003

Spectroscopic and Surface Analytical Studies of Gramicidin A in a Model Membrane

Barbara Goodall, Annia Kycia, Thamara Laredo, and Jacek Lipkowski
University of Guelph
50 Stone Road East, Guelph, ON, N1G 2W1
bgoodall@uoguelph.ca

The complex interactions between lipid membranes and proteins are a subject of interest in research fields investigating both fundamental properties and practical applications. The aim of this project is to investigate the properties of gramicidin A in a model membrane. Gramicidin A is a small 15 amino acid peptide that dimerizes in a bilayer lipid membrane to form an ion transport channel. Many studies investigating the physical properties of proteins and membranes have been achieved through the use of solid supported lipid membranes (sBLM). This study will investigate a sBLM comprised of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) and gramicidin A deposited on a hydrophilic thioglucose modified Au(111) electrode. A novel "floating" bilayer lipid membrane (f-BLM) will also be introduced which was designed to allow for a more dynamic and fluid model than the sBLM. The floating bilayer in this study is composed of DMPC, cholesterol, glycolipid monosialoganglioside (GM1), and gramicidin A deposited on a thioglucose modified Au(111) electrode. The GM1 is used as a spacer molecule to create a water reservoir between the modified electrode and lipid bilayer. The model membranes will be analyzed with atomic force microscopy (AFM) and polarization modulation infrared reflection absorption spectroscopy (PMIRRAS). The AFM studies will provide information about the distribution of the components in the model membranes, whereas PMIRRAS will probe the electric field driven changes in the orientation and conformation of gramicidin A in the lipid bilayer.

s2-004

Diketopyrrole-Pyrrole (DPP) Derivatives: Comparison of Electrochemical and in situ Spectroelectrochimal Experiment with DFT Simulations

Mieczyslaw Lapkowski[1], Pawel Zassowski[1], Aleksandra Kurowska[1], Sandra Pluczyk[1],Przemyslaw Data[1], Rafal Jedrysiak[1], Michal Czwartosz[1]
[1]Silesian University of Technology, Faculty of Chemistry
Strzody 9, 44-100 Gliwice, Poland
mieczyslaw.lapkowski@polsl.pl

Diketopyrrole-pyrrole derivatives are attracting considerable attention among scientist due to their interesting spectroscopic and electrochemical properties. Among them, ability of reversible oxidation and reduction of those compounds allows for spectroscopic characterization of charged species.

In this work, we report comparison of results for model diketopyrrole-pyrrole derivatives (fig.1): electrochemical (cyclic voltammetry) and *in situ* spectroelectrochemical (UV-Vis-Nir and Electron Paramagnetic Resonance) experiments with Density Functional Theory calculations. Based on those investigations, conclusions are made about the electronic structure of both neutral and charged species. In case of neutral molecules parameters such as position of HOMO and LUMO levels are given. For charged species, information about spin density distribution and optical transitions are presented.

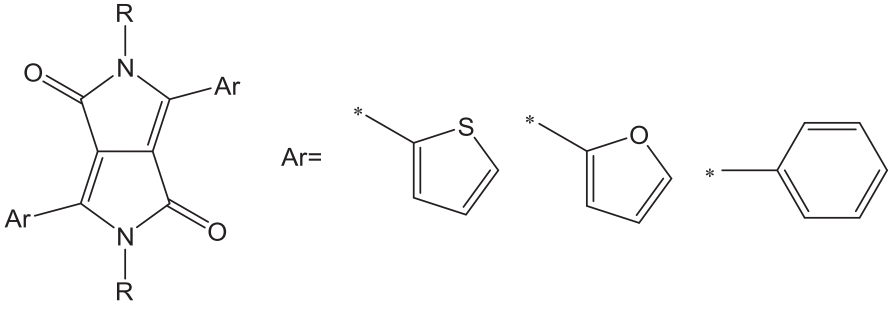


Fig. 1 – Compounds investigated in this study

s2-005

Spectroelectrochemical and Electrochemical Properties of Novel Ruthenium Phthalocyanines Biaxially Ligated with Pyridine Derivatives

Piotr Pander[1], Katarzyna Laba[1,2], Przemyslaw Data[1,2], Mieczyslaw Lapkowski[1,2]
[1] Silesian University of Technology, Faculty of Chemistry, Department of Physical Chemistry and Technology of Polymers, 44-100 Gliwice, Strzody 9, Poland
[2] Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, Zabrze, Poland
PanderPiotr@gmail.com

Phthalocyanines (Pcs) and their metal complexes (MPcs) have been extensively investigated for various applications, due to their special properties, such as strong delocalized 18-π electron aromatic system, good thermal stability and interesting optical properties[1,2]. Their physicochemical properties can be easy modified through synthetic manipulation by modifications of the benzene rings substituents, variation of the central metal ion and insertion of a substituent as an axial ligand. Unsubstituted Pcs are generally difficult to dissolve in most organic solvents, hence, limiting their further applications[3]. Among MPcs, ruthenium phthalocyanines are especially interesting because of efficient triplet state generation and photoinduced charge transfer, as well as strong binding of axial ligands, which enable coupling to other functional moieties[4].

The investigated MPcs are peripheral octa-substituted ruthenium phthalocyanines bisaxially ligated with pyridine derivatives. Herein we will present the electrochemical and spectroelectrochemical investigations to discuss the properties of ruthenium phthalocyanines as well as the ligands.

Acknowledgements. This work was supported by National Science Centre, Project No. 2011/03/B/ST5/01475.

References

1. M. Arıcı, D. Arıcan, A. L. Uğur, A. Erdoğmuş, A. Koca, Electrochimica Acta, 87, 554– 566, (2013)
2. C. Yağcı, A. Bilgin, Polyhedron, 51, 142–155, (2013)
3. K. S. Lokesh, A. Adriaens, Dyes and Pigments, 96, 269-277, (2013)
4. T. Rawling, A. McDonagh, Coord. Chem. Rev. 251, 1128-1157, (2007)

s2-006

Determining the Structure and Orientation of the Alamethicin Ion Channel in the Opened and Closed States in Lipid Matrices using ATR and Electrochemical PMIRRAS

Muzaffar Shodiev, Jay Leitch, Ryan Seenath, Michael Grossutti, Jacek Lipkowski
Department of Chemistry, University of Guelph
50 Stone Road East, Guelph, Ontario, N1G 2W1 Canada
mshodiev@uoguelph.ca

Alamethicin is a short antibiotic peptide produced by the fungus Trichoderma viride. This peptide consists of 20 residues and is capable of forming ion channels in biological membranes. These ion channels are voltage-gated due to their large molecular dipoles. The mechanisms behind channel formation and opening and closing have remained controversial due to the complexity of biological membranes. Therefore, model membranes will be used to study these two mechanisms.

The goals of this project are to monitor the incorporation of Alamethicin into diphytanoyl-phosphatidylcholine (DPhPC) model biomimetic membranes and characterize the opening and closing of these incorporated Alamethicin channels. Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) will be employed to elucidate mechanism of Alamethicin incorporation by first fusing vesicles to the ATR prism and then injecting Alamethicin into the bulk solution. The amide I band will be examined to determine both the rate of insertion and orientation of the peptides as a function of time. In order to determine the opening and closing of the alamethicin pore, a mixed model bilayer containing Alamethicin will be deposited onto the surface of a Au(111) electrode. The voltage applied to the electrode surface will mimic the transmembrane potential observed in biological systems. PMIRRAS will be used to examine changes in the structure and orientation of the Alamethicin peptides as a function of the applied potential. This data will provide insight into the processes responsible for channel opening and closing and compared with pre-existing crystal structures to find the model of best fit.

s2-007

Electrochemical and PM-IRRAS studies of valinomycin ionophores in a tethered bilayer lipid membrane

Zhangfei Su, Adrian L. Schwan, Jacek Lipkowski*
Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada
E-mail: jlipkows@uoguelph.ca

Valinomycin is a cyclodepsipeptide that can form ionophores in both biological and synthetic membranes. It can selectively complex with and transport potassium cation across the membrane. In the present paper, electrochemical and the photon polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) techniques were used to study the valinomycin ionophores in a using tethered bilayer lipid membrane (tBLM) in which a thiolipid 2,3-di-*O*-phytanyl-*sn*-glycerol-1-tetraethyleneglycol-DL-α-lipoic acid ester (DPTL) was used as the proximal leaflet (tethered to the metal) and 1,2-diphytanoyl-*sn*-glycero-3-phosphocholine (DPhPC) as the distant leaflet (in contact with solution). The electrochemical results show that after incorporating valinomycin into the tBLM, the double layer capacity increases and the membrane resistance decreases, confirming that valinomycin form ionophores in the tBLM. PM-IRRAS spectra in $KClO_4$ solution displayed strong amide I band between 1650 ~ 1660 cm^{-1}, which corresponds to the potassium complex of valinomycin. With the help of independently measured transmission spectrum of valinomycin the orientation of the peptide in the tethered bilayer was determined.

s3-001

Analysis of the Nanocurrents Generated on AISI 304 due to Pitting Corrosion by means of SECM

J. García-Antón, R.M. Fernández-Domene, R. Sánchez-Tovar
Ingeniería Electroquímica y Corrosión, Departamento de Ingeniería Química y Nuclear, Universitat Politècnica de València, Camino de Vera s/n, 46022 Valencia, Spain
jgarciaa@iqn.upv.es

Scanning electrochemical microscopy (SECM) has become a powerful technique for quantitative investigations of interfacial physicochemical processes, in a wide variety of areas. Pitting corrosion is a localized type of corrosion commonly observed on stainless steels in the presence of aggressive ions, such as chlorides. SECM permits studying the formation and evolution of stable pits by monitoring the nanocurrents arising from them.

In this work, stable pits have been generated on a passivated AISI 304 surface imposing an anodic potential in a sodium chloride solution. Nanocurrents from the AISI 304 surface were measured with a 25 microns platinum tip using oxygen as intermediate.

Images of the pits formed on the stainless steel surface were obtained in situ by SECM (Figure 1). Laser Scanning Confocal Microscopy (LSCM) was used to characterize the pits morphology and dimensions.

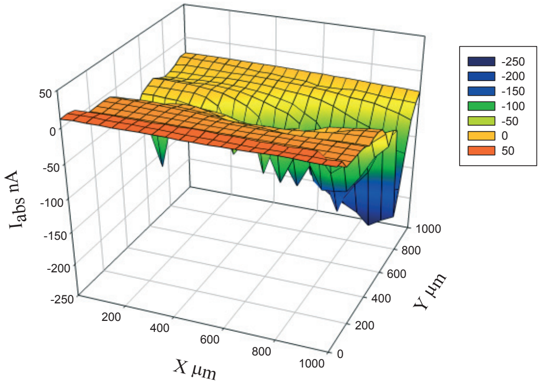


Figure 1. Image of a pit formation on the AISI 304 characterized using SECM.

s3-002

Preparation of SECM Nanoelectrodes Using Heating Coil Puller

Wojciech Nogala, Justyna Jedraszko, Magdalena Kominiak,
Martin Jönsson-Niedziolka, Marcin Opallo
Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44/52, 01-224 Warsaw, Poland
wnogala@ichf.edu.pl

Nanometer-sized electrodes are utilized to research in many laboratories worldwide. They were used to study electrochemical and biological systems on the nanoscale including electrochemistry of single redox molecules,[1] single nanoparticles[2] as well as processes inside biological cells.[3]

Besides a number of nanolithographic methods of nanoelectrode fabrication,[4] one of the most interesting from a practical point of view is sealing of metallic microwire into glass capillary followed by laser assisted pulling and polishing.[5] Such electrodes are usable as scanning electrochemical microscopy (SECM) nanotips, intracellular nanosensors and can be easily renewed by polishing. For fabrication of platinum glass-sealed nanoelectrodes laser-based pullers were used in order to melt Pt-microwire.

We found that platinum microwire covered by heat-softened borosilicate glass is malleable enough to pull it to nanowire at temperatures much below Pt melting point. Utilizing this phenomenon, we developed a new method of platinum SECM nanotips fabrication which does not require laser-assisted pulling. For sealing and pulling we used micropipette puller equipped with heating coil. Such an apparatus, contrary to laser-based pullers, is easily attainable by every laboratory around the world. Obtained nanoelectrodes were characterized by voltammetry, SECM, scanning electron microscopy and atomic force microscopy.

References:

[1] P. Sun, M. V. Mirkin, J. Am. Chem. Soc. 130 (2008) 8241.
[2] Y Li, J. T. Cox, B. Zhang, J. Am. Chem. Soc. 132 (2010) 3047.
[3] Y. Wang, J-M. Noël,J. Velmurugan, W.Nogala, M. V.Mirkin, C. Lu, M. G. Collignon, F. Lemaître, C. Amatore, Proc. Natl. Acad. Sci. U. S. A. 109 (2012) 11534.
[4] S. M. Oja, M. Wood, B. Zhang, Anal. Chem. 85 (2013) 473.
[5] Shao, Y.; Mirkin, M. V.; Fish, G.; Kokotov, S.; Palanker, D.; Lewis, A. Anal. Chem. 69 (1997) 1627.

s4-001

Some Catalytic Properties of Intermetallic Compounds

Leandro Moreira de Campos Pinto[a,b] and Wolfgang Schmickler[b]
[a]*Instituto de Química, Universidade Federal do Mato Grosso do Sul, 79.074-460 Campo Grande, Brazil*
[b]*Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany*
leandro.moreira@uni-ulm.de

The wide and effective implementation of fuel cells is still limited by the lack of efficient, cheap and robust catalysts. In spite of an intensive search for alternative materials, the best catalysts available are still based on platinum and similar noble metals. Besides their high costs, these materials have another disadvantage when used in the anode of the device: they are susceptible to poisoning by CO [1, 2]. Carbon monoxide has been extensively reported as a potential poison that dramatically decreases the lifetime of Pt electrocatalysts [1–3]. In general, CO is present as result of the incomplete oxidation of organic molecules and even found as trace contaminant in hydrogen gas when the latter is obtained from catalytic reforming [3]. In this study a series of ordered intermetallic compounds of Sn with noble metals – AuSn, PdSn, and PtSn – has been investigated as prospective materials for hydrogen catalysis. Such materials are interesting in view of their homogeneity, structural and electronic properties quite distinct from their single constituents, and great reproducibility [4]. Likewise, they have been addressed as CO-tolerant materials. Among the studied intermetallic compounds PtSn is the most promising one and can be employed as an alternative instead of pure Pt catalysts, as it presents good activity toward hydrogen oxidation reaction, evaluated both by electrochemical measurements and theoretical methods [5]. Furthermore, according to our calculations all intermetallic compounds were considered tolerant against CO [6].

[1] T. Iwasita, Electrochim. Acta, 47 (2002) 3663.
[2] Z. Ji and J.-Q. Li, Chem. Phys. Lett., 424 (2006) 111.
[3] N. de-los-Santos-Álvarez, L.R. Alden, E. Rus, H. Wang, F.J. DiSalvo, and H.D. Abruña, J. Electroanal. Chem., 626 (2009) 14.
[4] L.M.C. Pinto, E.R. Silva, R. Caram, G. Tremiliosi-Filho, and A.C.D. Ângelo, Intermetallics, 16 (2008) 246.
[5] E. Santos, L.M.C. Pinto, G. Soldano, A.F. Innocente, A.C.D. Ângelo, and W. Schmickler, Catal. Today, 202 (2013) 191.
[6] L.M.C. Pinto, M.F. Juárez, A.C.D. Ângelo, and W. Schmickler, Electrochim. Acta, 116 (2014) 39.

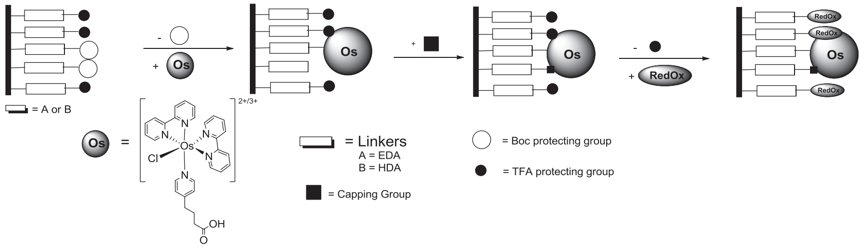
s5-001

Toward the Control of Partial Covalent Modification of Glassy Carbon Surfaces Using Osmium Bipyridyl Complexes as Redox Centres.

Jessica Groppi, Philip N. Bartlett, Jeremy D. Kilburn
Queen Mary University of London
Joseph Priestley Building, Mile End Road, E1 4NS, London, UK
j.groppi@qmul.co.uk

The patterning of surfaces with control over the relative ratios of different components represents one of the goals in the creation of devices for biosensing and energy storage, since it could improve the stability and sensitivity of the response. Considering this, a general methodology for the creation of controlled mixed monolayers on glassy carbon (GC) surfaces was developed, using osmium bipyridyl complexes and anthraquinone as model redox probes, but potentially applicable to more complex systems.

The work consisted in the electrochemical grafting on GC of a mixture of diamine linkers in different ratios and characterised by protecting groups which allowed orthogonal deprotection. After optimisation of the deprotection conditions, it was possible to selectively remove one of the protecting groups, couple a suitable osmium complex and cap the residual free amines. The removal of the second protecting group allowed the coupling of anthraquinone. The characterisation of the surfaces by cyclic voltammetry showed the variation of the surface coverage of the two redox centres in relation to the initial ratio of the linking amine in solution. It was then possible to build patterned surfaces where the osmium complex acted as mediator for Glucose dehydrogenase (GDH), covalently bonded to GC through an exposed cysteine residue to a maleimide moiety.



s5-002

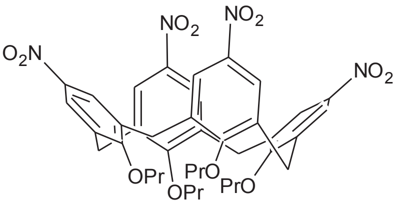
Electrochemical generation of stable oligo-radical anions of mono-, di-, tri- and tetranitrocalix[4]arenes

Jiří Ludvík, Alan Liška, Jiří Klíma,
J. Heyrovský Institute of Physical Chemistry of the AS CR, v.v.i., Dolejskova 3,
182 23 Prague 8, Czech Republic, E-mail: jiri.ludvik@jh-inst.cas.cz

A series of mono-, di-, tri- and tetranitro calix[4]arenes is an example of a molecule with multiple redox centers, mutual interaction of which is to be studied. This type of compounds represent a suitable inert and stable frame for building "smart" molecules and supramolecular assemblies, since the reducible nitro groups located at the upper rim are promising precursors for electrosynthetic formation of pendant arms.

In this work a series of mono-, di-, tri- and tetra nitroderivatives was reduced, the sequence of individual steps was described and the mechanism discussed. It was found that in this molecule with several redox centers all nitro groups are electronically isolated and thus are reduced independently yielding stable mono-, di-, tri- and tetra-radical mono-, di-, tri- and tetra-anions, respectively. Two different couples of equivalent nitro groups were found in tetranitro derivatives, therefore the molecule must have a "pinched" shape even in solution [1]. The simultaneous recording of EPR and UV-VIS spectra with the passed charge during electrolyses proved the presence of stable oligo-radical oligo-anions.

It was found, that the reduced (tetra)nitro calix[4]arenes have coordination abilities towards alkali-metal cations [2].



Acknowledgement: The authors thank prof. P.Lhoták (Prague Institute of Chemical Technology) and prof. P.Vojtíšek (Charles University Prague) for granting the compounds and prof. A. Fry (Wesleyan University USA) for quantum chemical calculations. The financial support of the project was provided by the grant GAČR 13-21704S (Grant Agency of the Czech Republic).

References:

[1] A. Liška,, P. Vojtíšek, A.J. Fry and J. Ludvík, J. Org Chem in print 2013; http://dx.doi.org/10.1021/jo4015613
[2] A. Liška *et al.,* to be submitted

s5-003

Investigation of Electrochemical Reaction Mechanism of Acid Black 1 (C.I. 20470) by using Voltammetric Techniques

Necati MENEK[1], Serpil ZEYREKLİ[1] Saim TOPÇU[2] and Yeliz KARAMAN[3]
[1]Ondokuz Mayıs University, Sci. and Arts Fac., Depart. of Chem., 55139, Kurupelit, Samsun, Turkey
[2]Giresun University, Sci. and Arts Fac., Depart. of Chem, Giresun, Turkey
[3]Sinop University, Sci. and Arts Fac., Depart. of Chem, 57000 Sinop, Turkey
e-mail: nmenek@omu.edu.tr

Azo compounds all have the same functional group -N=N-, which is a chromophore. So many kinds of them are common dyes for food, pharmaceuticals beverages and textile industry as coloring agents, biomedical studies, advanced application in organic synthesis and high technology areas as laser, liquid crystaline displays, electro-optical devices and ink-jet printers.. Thus, it appears necessary to identify and quantify with accuracy the dyes present demonstrate the need for developing fast, accurate and selective techniques for synthetic dyes analysis The aim of this study is to investigate comparatively of electrochemical properties of Acid Black 1 (C.I. 20470, 4-amino-5-hydroxy-3-(4-nitro-phenyl-azo)-6-phenylazo-naphthalene-2,7-disulfonic acid) in different electrodes by using different techniques.

The polarographic and voltammetric experiments were performed using a computer controlled electroanalysis system (Metrohm 757 VA Computrace Electrochemical Analyser). A three electrode combination system was used. This consisted of a Multi Mode Electrode (DME, SMDE and HMDE), an Ag/AgCl reference electrode and a Pt wire auxiliary electrode. All measurements were carried out at room temperature.

There are three electroactive groups at azo dyes. Two of these are azo groups, the other is the nitro group. Two cathodic peaks are formed in Acid Black 1. First of these is belong to azo group and second of these is belong to the other azo and nitro groups are determined. Irreversible electrode reaction mechanism was observed for the azo dyes. The peak potential of reduction peak depends on pH and shifted to more negative potentials with increase in pH indicates that proton involves in rate-determining step. As a result, total electrode reaction mechanism is suggested for dye from the experimental data.

References

[1] J.P. Hart, W.F. Smyth, "*The Analyst*", 105, 929, 1980.
[2] Y.Karaman N. Menek *J Electrochem Soc* 2012;159(10):H805-10.
[3] N. Menek. *Anal Lett* 1998;31:275-82.
[4]J.Barek, D.Civisova, A.Ghosh, J.Zima, *J.Collect. Czech Chem. Commun.* 1990;55:379-90.

s5-004

Composite SPEEK Polymer Membranes with Acidic Ionic Liquids

G.Vaivars[1,2] , E.Sprugis[1,2], J.Kleperis[2]
[1]*University of Latvia, Department of Chemistry*
Kr.Valdemara 48, LV-1013, Latvia
[2]*University of Latvia, Institute of Solid State Physics*
Kengaraga 8, LV-1063, Latvia
e-mail address: Guntars.Vaivars@cfi.lu.lv

In ionic devices the medium temperature range (100-200ºC) is attractive from practical point view of application. Ionic liquids are suitable for composite formation due to high temperature and electrochemical stability.

Following acidic ionic liquids were used for composite preparation: 3-(1-pyridinio)-1-propanesulfonate [PyPS] hydrogen sulfate (1a), dihydrogen phosphate (1b) and p-toluenesulfonate (1c), 3-(1-methyl-3-imidazolio)-1-propane¬sulfonate [MeImPS] hydrogen sulfate (2a), dihydrogen phosphate (2b) and p-toluenesulfonate (2c) as well as 3-(1-butyl-3-imidazolio)-1-propane¬sulfonate [BuImPS] hydrogen sulfate (3a), dihydrogen phosphate (3b) and p-toluenesulfonate (3c) [1]. The casting and impregnation was used for ionic liquid/SPEEK (sulphonated polyether ether ketone) composite formation. Double cross-linked SPEEK polymer prepared according to [2].

Structures of ionic liquids obtained in this work have been determined by ^{1}H NMR and XRD, but water content by Karl Fischer method. Thermal stability of ionic liquids and membranes was controlled by thermogravimetry analysis. Conductivity was obtained from impedance measurements using Autolab set-up in temperature range 20-140ºC. Equivalent circuit method was used for detailed interface studies.

[1] L.Lasmane, E.Ausekle, A.Priksane, G.Vaivars. Acidic ionic liquids as composite forming additives for ion-conducting materials // IOP Conf Ser: Mat Sc Eng 49 (2013) 012039.
[2] H.Luo, G.Vaivars, J.Kleperis. A novel double cross-linked proton conducting membrane and the methods. Latvian patent Nr. 13960 (2009).

s5-005

Impedance Analysis of Acidic Ionic Liquids

G.Vaivars[1,2] , E.Ausekle[1], A.Zekunde[1], A.Priksane[1]
[1]*University of Latvia, Department of Chemistry*
Kr.Valdemara 48, LV-1013, Latvia
[2]*University of Latvia, Institute of Solid State Physics*
Kengaraga 8, LV-1063, Latvia
e-mail address: Guntars.Vaivars@cfi.lu.lv

In alternative energy devices the medium temperature polymer electrolyte membrane (PEM) fuel cells are of growing importance. It resulted in rising interest in field of ionic liquids as components for polymer membranes due to higher temperature (100-200°C) and electrochemical stability.

Acidic ionic liquids synthesized and examined in this work include 3-(1-pyridinio)-1-propanesulfonate [PyPS] hydrogen sulfate (1a), dihydrogen phosphate (1b) and p-toluenesulfonate (1c), 3-(1-methyl-3-imidazolio)-1-propane¬sulfonate [MeImPS] hydrogen sulfate (2a), dihydrogen phosphate (2b) and p-toluenesulfonate (2c) as well as 3-(1-butyl-3-imidazolio)-1-propane¬sulfonate [BuImPS] hydrogen sulfate (3a), dihydrogen phosphate (3b) and p-toluenesulfonate (3c). Impedance analysis was using equivalent circuit method to characterize the impact of small water impurities.

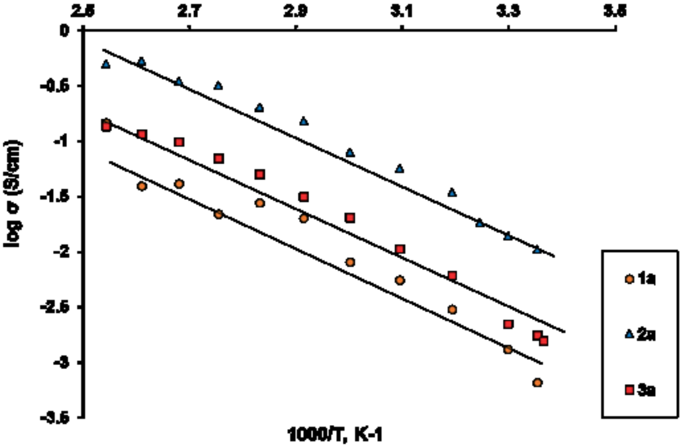


Figure 1. Arrhenius plot for ionic liquid's with different cations.

s6-001

Electrochemical Characterization of RuO_2 nanocomposite under Hydrogen Evolution Reaction

D. Abirami, M.V. Sivaiah, H.G. Ang
*Energetics Research Institute (E**n**RI), Nanyang Technological University,*
Block N1-B4a-02, Nanyang Avenue, NTU, Singapore 639798
Tel : (65) 6592 1814; Fax: (65) 6792 7173; abiramids@ntu.edu.sg

RuO_2 as the cathode material for hydrogen evolution reaction (HER) gaining more importance because of is chemical stability even under strong reduction conditions. Earlier studies on RuO_2 as electrocatalyst for HER shown that chemisorptions of hydrogen atoms in RuO_2 structure favors the activity and prolong use of RuO_2 leads to diffusion of hydrogen atoms to substrate, namely Ti and formation of Ti-hydride leads to instability of RuO_2 coating [1-3]. However, structural changes in hydrous RuO_2 (with more structural water) during HER reaction are not studied so far. In this study, RuO_2 nanocomposite (nanocrystals of rutile structure with water molecule at the boundaries) are synthesized by varying structural water and characterized electrochemically (Electrochemical impedance spectroscopy (EIS), I/E curves, cyclic voltammetry) under HER conditions. Figure 1 illustrates the EIS spectra of RuO_2 nanocomposite with moderate structural water in 1M NaOH medium. EIS measurement allows in-situ evaluation of structural feature of materials and the results obtained in basic and acidic medium will be presented in light of structural changes in RuO_2 nanocomposite during HER.

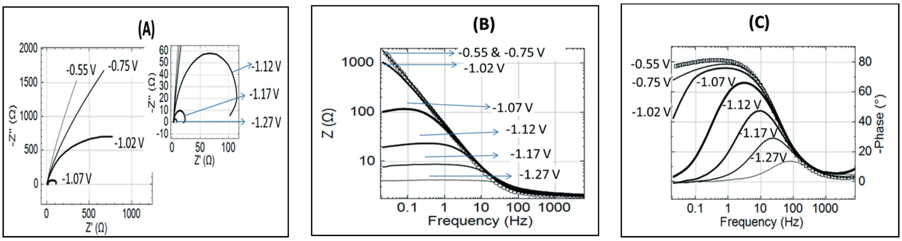


Figure 1. Nyquist(A), Bode modulus(B) and Bode phase(C) plots of RuO_2 nanocomposite with moderate structural water molecule under HER conditions in 1M NaOH. The plots recorded at varying DC potential (vs SCE) and 50 $mV_{(RMS)}$ of AC signal . Ink consists of sample and nafion® 117 deposited on Ti-rod (0.5 cm^2)

References
1. C. Chabanier and D. Guay, J. Electroanal. Chem. 570 (2004) 13.
2. A. Cornell and D. Simonsson, J. Electrochem. Soc. 140 (1993) 3123.
3. I. Paseka, CI&CEQ, 1 (2005) 114.

s6-002

Effects of Temperature on Electrochemical Dissolution of Nickel in Ionic Liquids

Mona Amiri, Maduraiveeran Govindhan, Aicheng Chen
Department of Chemistry, Lakehead University,
955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada
mamiri@lakeheadu.ca, achen@lakeheadu.ca

Nickel is used in various industries, lots of which are involved with dissolving or depositing processes in different electrolytes. Therefore, it has been the subject of many investigations regarding nickel dissolution and passivation in acid and neutral mediums using different electrochemical techniques. However, there is a few data available on the dissolution behavior of nickel in ionic liquids, which have received a great deal of attention during past two decades due to their properties such as thermal stability, ion conductivity and being liquid at temperatures below 100^{o}C.

The electrochemical behavior of Nickel dissolution in 1-butyl-3-methyl-imidazolium chloride (BMIC) containing different amounts of chloride salts has been investigated at 4 different temperatures using linear voltammetry, X-ray diffraction (XRD) and Scanning electron microscopy (SEM) analysis of the surface. It has been shown that the dissolution rate of the nickel increases with the increase in temperature. The surface analysis shows that dissolution occurs via formation of some small pits on the surface most probably due to chloride ions presence in the solutions.

References
[1] J. Gregori, J. J. Garcia-Jareno, D. Gimenez-Romero, A. Roig, F. Vicente, *J. Electrochem. Soc.* 154 (2007) 371-377.
[2] Q. Zhang, Y. Hua, Z. Zhou, *Int. J. Electrochem. Sci.* 8 (2013) 10239 – 10249.

s6-003

A new process for direct in situ sonolectrochemical synthesis of PPy-Au nanocaomposite coating and study of its corrosion protection performance

H. Ashassi-Sorkhabi*a, R. Bagheri a, B. Rezaie-moghadam a
a) Electrochemistry Researches Laboratory, Department of Physical Chemistry,
Faculty of Chemistry, University of Tabriz, Tabriz, Iran
ashassi@tabrizu.ac.ir, habib.ashassi@gmail.com

The Polypyrrole (PPy) and Polypyrrole-Au (PPy-Au) nanocomposite films have been sonoelectrochemically synthesized on St-12 steel electrode using galvanostatic technique. The synthesis solution was prepared by dissolving the pyrrole and chloroauric acid (HAuCl4) in an aqueous oxalic acid solution. Experimental design according to Taguchi method has been applied to optimize the factors on the synthesis of PPy-Au nanocomposite coating. Three factors that were used to design an orthogonal array L9 are: Synthesis time (t), Current density (I) and Concentration of HAuCl4 (C). The synthesized Au nanoparticles during nanocomposite polymerization were characterized by UV-visible spectroscopy.

The morphological characterization of the coatings was carried out by scanning electron microscopy (SEM). The SEM images of PPy show smooth surface while PPy-Au nanocomposite film has a compact and nonporous morphology. The corrosion protection of coatings was investigated by open circuit potential (OCP) time trends, potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS) in NaCl 3.5% solution. The results showed that the nanocomposite coatings ensured good protection against corrosion. On the other hand, such nanocomposite coatings act as a physical barrier against corrosive species.

Key words: Sonoelectrochemistry, Corrosion, Polypyrrole, Au-Nanocomposite, EIS, Taguchi Design of experiments.

Reference

[4] H. Jeon, J. Park, M. Shon, Corrosion protection by epoxy coating containing multi-walled carbon nanotubes, J. Ind. Eng. Chem. 19 (2013) 849-853.

[5] H.N.T. Le, B. Garcia, C. Deslouis, Q.L. Xuan, Corrosion protection and conducting polymers: polypyrrole films on iron, Electrochim. Acta 46 (2001) 4259-4272.

[6] P. Ocon, A.B. Cristobal, P. Herrasti, E. Fatas, Corrosion performance of conducting polymer coatings applied on mild steel, Corros. Sci. 47 (2005) 649.

[7] T. ohtsuka, corrosion protection of steel by conducting polymer coating, International Journal of Corosion (2012).

s6-004

Studies of $LiFePO_4$ Cathode – Electrolyte Interface

Gunars Bajars, Karina Bikova, Gints Kucinskis, Janis Kleperis, Andrejs Lusis
Institute of Solid State Physics, University of Latvia
8 Kengaraga street, Riga, LV-1063, Latvia
gunars.bajars@gmail.com

With an increasing demand for improved energy storage, the research of lithium ion battery technology in general [1] and cathode material particularly [2] becoming more and more important. In this work $LiFePO_4$ cathode – electrolyte interface was studied, focusing on the surface of the cathode for $LiFePO_4$/C and $LiFePO_4$/C/graphene bulk material and $LiFePO_4$ thin films. The increase of cathode surface area can improve the rate performance of the cell considerably, thus enable to achieve faster battery charge and discharge times.

$LiFePO_4$/C and $LiFePO_4$/graphene bulk material have been prepared by solid-state reaction. After structural and morphological characterization by XRD and SEM the electrochemical test cell with $LiFePO_4$ cathode, metallic lithium anode and $LiPF_6$ electrolyte was assembled. $LiFePO_4$ thin films have been obtained by radio frequency magnetron sputtering [3]. The electrode – electrolyte interface has been characterized with electrochemical impedance spectroscopy (EIS), determining charge transfer resistance and electric double-layer capacity as well as lithium ion diffusion coefficients.

It was found that graphene additive increases not only the electron conductivity of the bulk material, but also electrical double layer capacitance, thus indicating more developed electrode surface area. Charge transfer resistance, electrical double layer capacity and lithium ion diffusion coefficients have been determined at various charge and discharge rates both for bulk material and thin films. It was determined that charge transfer resistance has a minimum value at the equilibrium state (3.45 V) with electrical double layer capacitance and lithium ion diffusion coefficients being significantly lower for thin films than for bulk materials.

[1] L. Lu, X. Han, J. Li, J. Hua, M. Ouyang, J. Power Sources 226 (2013) 272.
[2] G. Kucinskis, G. Bajars, J. Kleperis, J. Power Sources 240 (2013) 66.
[3] G. Bajars, G. Kucinskis, J. Smits, J. Kleperis, Solid State Ionics 188 (2011) 156.

s6-005

Photocatalytic Activity of Ferrite Based Nanoparticles, Their Clusters and Thin Films for Solar Water Splitting

Martins Vanags[1], Gunars Bajars[1], Andris Sutka[2], Liga Grinberga[1], Janis Kleperis[1],
Ineta Liepina[3]
[1]Institute of Solid State Physics, University of Latvia
Kengaraga 8, Riga, LV-1063, Latvia
[2]Institute of Silicate Materials, Riga Technical university
Azenes 14/24, Riga, LV-1048, Latvia
[3]Faculty of Chemistry, University of Latvia
Kr.Valdemāra 48, Riga, LV-1013, Latvia
gunars.bajars@lu.lv

Light induced charge transport and following catalytic splitting of water molecules in nanoparticle based materials promises efficient and sustainable pathway for H_2 production from water. Particularly nanoparticles based on α-Fe_2O_3 are of interest in solar-to-hydrogen energy conversion.

In this investigation, several un-doped and doped ferrite nanomaterials were synthesized using sol-gel auto-combustion, sol-gel, spray-pyrolysis and electrophoresis techniques. Specific efforts were applied to obtain samples in the form of separate nanoparticles, clusters with defined dimensions and thin films.

Synthesized materials were characterized using powder X-ray diffraction, BET surface area analysis, scanning electron microscopy, transmission electron microscopy, light absorption and infrared spectroscopy (FTIR, Raman) techniques. To compare the photoactivity of samples, photodegradation of methylene blue was chosen.

It is shown that photocatalytic activity is depending from the dimensions of nanoparticles and clusters, as well as from selected dopants.

s6-006

Methanol oxidation on Pt/CNT electrocatalysts promoted with TiO_2

Z. Bedolla[1], Y. Verde[2], Y. Gochi[3], G. Alonso[1]
[1]Centro de Nanociencias y Nanotecnología, Km 107 Carretera Tijuana-Ensenada,
C.P. 22800, Ensenada, B. C., México.
zairabe@cnyn.unam.mx
[2]Instituto Tecnológico de Cancún, Av. Kabah Km. 3, C.P. 77500, Cancún,
Quintana Roo, México.
[3]InstitutoTecnologico de Oaxaca, Av. Ing. Víctor Bravo Ahuja No. 125, C.P.
68030, Oaxaca, México.

Electrocatalytic materials are a major challenge for Direct Methanol Fuel Cells (DMFC) commercialization. To improve the properties of supported Pt electrocatalysts, various metal oxides are used to enhance the methanol oxidation performance [1-3]. Currently, titanium oxide is widely studied as electrocatalytic promoter due to its low cost and stability in acid media [1-3].

In this research, Pt-$x$$TiO_2$/CNT electrocatalysts with various titanium oxide loadings (x= 5, 10 and 20 wt%) were prepared. In first instance, the titanium oxide was incorporated to CNT by a sonochemical method to obtain the system TiO_2/CNT. Then, 10 wt% of Pt nanoparticles were incorporated to TiO_2/CNT by sonochemical conditions using $NaBH_4$ as a reducing agent.

The chemical composition of the systems was determinated by ICP analysis. The electrocatalysts structure was characterized by XRD diffraction and HRTEM. The nitrogen adsorption was performed to determinate the specific surface area by the BET method. The electrochemical study was performed by cyclic voltammetry in a three-electrode half-cell at room temperature.

Pt-$x$$TiO_2$/CNT electrocatalysts were successfully synthesized by a short time synthesis method. The results of the cyclic voltammetry test for the methanol oxidation suggest that the incorporation of TiO_2 in 10 wt% improves the electrocatalytic activity of the synthesized materials, in comparing to the system Pt/CNT.

References

[1]W. Xiuyu, Z. Jingchang, Z. Hong, Chin. J. Catal., 32 (2011), 74-79.
[2]W. Wang, H. Wang, J. Key, V. Link, *et al.*, Ionics, 19 (2013), 529-534
[3] P. Kolla, A. Smirnova, Int. J. Hydrogen Energy, (2013), 1-8.

s6-007

Significant Enhancement in the Electrochemical Catalytic Activity of Titanium Dioxide Nanotubes

Xin Chang, Sapanbir S. Thind, Jiali Wen, Aicheng Chen
Department of Chemistry, Lakehead University
955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada
xchang1@lakeheadu.ca

Titanium dioxide (TiO_2) is undeniably one of the most intensely studied semiconducting photocatalysts due to its unique combination of outstanding properties, such as biological and chemical inertness, high efficiency, low cost, environmental tolerance and high stability. In recent years, TiO_2 has demonstrated its superiority in the abatement of pollutants, leading to widespread applications in air purification, water disinfection and the remediation of hazardous organic wastes [1, 2]. However, minimal research has been conducted in the study of TiO_2 as an electrocatalyst, since its low electrical conductivity prevents its use as such. In this presentation, we report on the significant enhancement in the electrochemical activity of TiO_2 nanotubes.

In this study, TiO_2 nanotubes were treated via electrochemical reduction, where the effects of current and reduction time were investigated. The prepared samples were characterized by scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Electrochemical methods, UV–Visible absorbance spectroscopy and Total Organic Compound (TOC) Analyzer were employed to determine the enhanced electrochemical activity of the TiO_2 nanotubes. Our studies have shown that the oxidation of salicylic acid (SA) at treated TiO_2 nanotubes exhibited a much greater efficacy than a Pt electrode. Stability tests indicated that the electrochemically treated TiO_2 nanotubes were highly stable over the electrochemical oxidation of SA. In addition, the treated TiO_2 nanotubes could be regenerated by carrying out electrochemical reduction subsequent to their long term application to SA oxidation.

References:

[1] K. Yan, G. Wu, C. Jarvis, J. Wen, A. Chen, *Appl. Catal. B: Environ.* 148 (2014) 281-287.

[2] K. Pan, M. Tian, Z.-H. Jiang, B. Kjartanson, A. Chen, *Electrochim. Acta* 60 (2012) 147-153.

[3] S.S. Thind, G. Wu, A. Chen. *Appl. Catal. B: Environ.* 111 (2012) 38-45.

s6-008

Study of Interaction of CTAB with Au Single Crystal Electrodes Towards Understanding the Role of CTAB in Shape-Controlled Synthesis of Nanomaterials

Ling Chen, Chang-Deng Xu, Jin-Yu Ye, Chun-Hua Zhen, Shi-Gang Sun*
State Key Lab of Phys. Chem. Solid. Surf., College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian.361005.
e-mail address: sgsun@xmu.edu.cn

Au nanoparticles (NPs) feature unique physicochemical properties that include good catalytic properties for a variety of oxidation reactions. The performances of Au catalysts depend strongly on their size and surface structure that is determined by the shape of Au NPs. Thus, synthesis of Au NPs with well-defined shapes is extensively investigated over the past decade, in which the functional molecules such as stabilizers, capping agents, surfactants and additives, etc. are indispensable. Cetyltrimethylammonium bromide (CTAB) is often used as capping agent, and plays an key role in the synthesis of Au NPs. However, the mechanism of CTAB in shape-controlled synthesis of Au NPs is still elusive. One assumption consists in that the micelles of CTAB act as soft templates[1]; Other postulation is that the CTAB can preferentially adsorb on different facts of a seed crystal[2]. However, there are no direct experimental evidences in supporting these hypotheses up to now. The use of interfacial electrochemistry is very promising for this investigation[3], because the interaction of CTAB with single crystal electrode surface is analogous to those occurring on facets of a nanocrystal.

In this communication, the interaction of CTAB with well-defined Au single crystal surfaces was investigated by using cyclic voltammetry and in situ FTIR spectroscopy. The results demonstrate that both bromide and hexadecyltrimethylammonium (CTA^+) ions are coadsorbed on Au(111) and Au(100). The adsorption of CTA^+ is surface structure selective on both crystal facets. In the cyclic voltammograms, two pairs of stable sharp peaks related to carbon chain length appear on Au(111), while one pairs of small peak related to carbon chain length appears on Au(100) upon the adsorption of cationic surfactant. The study has thrown an insight into understanding the role of CTAB in the formation of anisotropic nanoparticles.

Acknowledgements. Financial supports from NSFC (grants: 21229301 and 21361140374) are highly acknowledged.

References:

1 Wei Z, et al. Langmuir, 2004 , 20 (26): 11301− 11304.
2. Garg N, et al. Langmuir , 2010 , 26 (12): 10271− 10276.
3. Chen D H, et al. Science China, 2012, 55(11): 2353–2358.

s6-009

The Electrochemical Graphene Surface Force Balance

Nico E. A. Cousens[1], Judy Britton[2], Susan Perkin[1]* and Nicole Grobert[2]
[1]*Department of Chemistry, Oxford University, South Parks Road, Oxford OX1 3QZ, UK.*
[2]*Department of Materials ,Parks Road, Oxford, OX1 3PH, UK*
** corresponding author: susan.perkin@chem.ox.ac.uk*

The structure of liquids at charged surfaces is governed by a combination of electrostatic and other molecular interactions. The ordinary Surface Force Balance is used to detect the interaction between atomically smooth and negatively charged mica sheets across thin films of liquids; the film thickness ranges from hundreds of nanometers down to a single ion/molecule diameter(1, 2). From the resulting oscillatory force profiles we can determine the layering structure of the liquids. However, this instrument is limited to one surface charge: the natural surface charge of mica. This poster describes a new instrument, the Graphene Surface Force Balance, which enables the study of liquids at the surface of graphene. Due to the conductivity of graphene, the surface potential of both surfaces confining the liquid can be controlled externally for the first time.

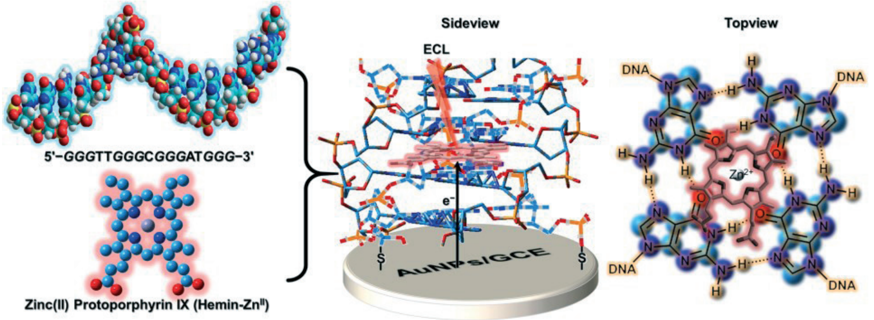
1. Perkin S, et al. (2011) Self-assembly in the electrical double layer of ionic liquids. Chemical Communications 47(23):6572-6574.
2. Smith AM, et al. (2013) Monolayer to Bilayer Structural Transition in Confined Pyrrolidinium-Based Ionic Liquids. The Journal of Physical Chemistry Letters 4(3):378-382.

s6-010

G-Quadruplex Promoted Electrogenerated Phosphorescence of Zinc(II) Protoporphyrin IX as DNAzyme for Molecular-Scale Signal Transduction

Tingting Zhang[†], Shengyuan Deng[†], Baojing Zhou[‡] and Dan Shan[†,*]
[†] *School of Environmental and Biological Engineering and* [‡] *School of Chemical Engineering, Nanjing University of Science and Technology*
Xiaolingwei No.200, Xuanwu District, Nanjing 210094, P.R. China
danshan@njust.edu.cn, sydeng@njust.edu.cn

Zinc(II) protoporphyrin IX (hemin-Zn^{II}) was found being capable of electrogenerated chemiluminescence (ECL) emission in the air-saturated aqueous solution at room temperature when stimulated at −1.75 V. However, the intensity was much stronger in the dipolar aprotic solvent like dichloromethane with tetrabutylammonium perchlorate as the supporting electrolyte than conventional phosphate buffer salines, since its molecular aggregation in aqueous solution causes electrochemically inactive dimers. Therefore, a guanine-rich sequence of single-stranded *oligo*-nucleotide was engineered as a kind of *anti*-hemin aptamer to accommodate the individual porphyrin into hemin-Zn^{II} *G*-quadruplex, resulting in an enhanced ECL performance. The transformation in secondary conformation and formation of this novel bioconjugate were monitored and validated via circular dichroism and UV-Vis absorption spectra. The ECL kinetics of hemin-Zn^{II} as well as hemin-Zn^{II} *G*-quadruplex were clarified by time-resolved photoluminescence spectroscopy with supplementary molecular simulation, that hemin-Zn^{II} experienced a singlet-triplet meta-state relaxation as transiting downward from the π-electron of porphine-occupied LUMO. Thus, a relatively slow-decay phosphorescence at 588 nm could be observed during the ECL of hemin-Zn^{II}. In addition, the endogenous dissolved oxygen was proved to be a potent coreactant for efficient ECL emission. This *G*-quadruplex-promoted electro-phosphorescence of porphyrin demonstrates a promising way for achieving functional DNAzyme analogues.



Scheme 1. Schematic illustration of the ECL emission of hemin-Zn^{II} *G*-quadruplex.

Reference

[1] J. M. Nicoludis, S. T. Miller, *et al.*, *J. Am. Chem. Soc.* **2012**, *134*, 20446−20456.
[2] V. Pradines and G. Pratviel, *Angew. Chem. Int. Ed.* **2013**, *52*, 2185−2188.

s6-011

Anodic Nanoesponges Formation in the Hydrodynamic Anodization of TiO_2

José García-Antón[1], Rita Sánchez-Tovar[1], Kiyoung Lee[2], Patrik Schmuki[2]
1 Ingeniería Electroquímica y Corrosión, Departamento de Ingeniería Química y Nuclear, Universitat Politècnica de València, Camino de Vera s/n, 46022 Valencia, Spain
2 Department of Materials Science and Engineering, WW4-LKO, University of Erlangen-Nuremberg, D-91058 Erlangen, Germany
jgarciaa@iqn.upv.es

Nanostructures are gaining increasing attention due to the advancements in material fabrication techniques and their unique properties, i.e. their nanosize, high surface area and porosity. These properties made nanostructures suitable for being used as photoelectrodes in photoelectrochemical applications. TiO_2 is one of the most studied oxides in materials science and it may find wide application in dye-sensitized solar cells, photocatalysis, biomedicine, and other related fields. Anodization of titanium is a useful technique to obtain a functional TiO_2 photoelectrode that does not need to be compacted or sintered onto a back contact. Anodization parameters, such as voltage, time, water content, temperature, pH and so on, have been widely evaluated during the last years, however, hydrodynamic conditions during anodization have not been studied in detail.

In this work, a new type of TiO_2 nanoestructure: "anodic nanoesponges" obtained by anodization under hydrodynamic conditions in glycerol, water and ammonium fluoride electrolytes have been analyzed. The study reveals that the morphology of the anodic nanosponges (Figure 1), with high surface area and a connected pathway for electrons is suitable for using this new nanostructure as photoelectrode in photoelectrochemical water splitting for hydrogen production.

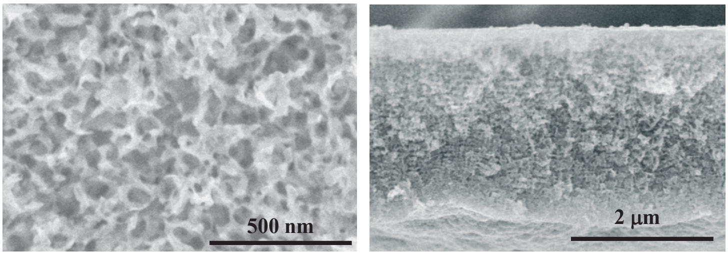


Figure 1. TiO_2 anodic nanosponges obtained by dynamic anodization.

s6-012

Synthesis and characterization of Pt/CeO_2 NT electrocatalyst for the oxygen reduction reaction

R.G. González Huerta[1*], S. Pacheco Espinoza[2], J. R. Vargas García[2]
[1]*ESIQIE-IPN, Laboratorio Electroquímica, UPALM México, D.F., CP 07738,*
[2]*ESIQIE- IPN, Depto de Metalurgia y Materiales, UPALM, México, DF, CP 07738*
**Tel +5255 57296000 ext 54246, e-mail: rosgonzalez_h@yahoo.com.mx*

The low durability of Pt/C electro-catalysts in polymer electrolyte membrane fuel cells (PEMFC), e.g., as a result of carbon oxidation to CO_2 in an acid medium, has been recognized as one of the most important hindrances to long-term stability. In this work, Pt electro-catalysts supported on CeO_2-nanotubes were prepared by VPI methods (Vapor Phase Impregnation). It had employed carbon nanotubes as a template to grow ceria nanotubes by a deposition liquid phase method. Finally ceria nanotubes were calcined at 450, 500 and 550°C under atmospheric conditions. The physical and electrochemical properties of Pt/ CeO_2-nanotubes (Pt/CeO_2 NT) were investigated by the characterization techniques of XRD, SEM and cyclic and linear voltammetry. The prepared materials were electrochemically evaluated in oxygen reduction reaction (ORR) at room temperature and acid medium. XR diffractogram shows characteristic peak of carbon nanotubes and CeO_2 when calcination temperature was 450 and 500°C, versus when calcination temperature was 550 °C carbon nanotubes signal disappeared and the CeO_2 phase is better define than calcination temperature was 450 and 500 °C. SEM CeO_2-NT image shows well define nanotubes and SEM Pt/CeO_2-NT image show well distributed Pt nanoparticles on CeO_2-NT. All electrochemical measurements were performed at 25°C in a single, conventional, three-electrode test electrochemical cell. The voltammogram graphic of Pt/CeO_2-NT showed the fingerprint electrochemical characteristics of platinum. Between 0.05 and 0.3 V/NHE, hydrogen adsorption/desorption zone is observed. On the anodic sweep above 0.8 V/NHE, an oxide film is formed on the surface of the platinum materials. The oxide film is removed during the cathodic sweep by the oxide reduction; between 0.3 and 0.6 V/NHE, the double-layer region is located. In ORR-polarization curves are defined tree zones, first is charge transfer control zone (0.9-0.85 V/NHE), the mixed-diffusion zone (0.85-0.6 V/NHE) and the mass transfer control zone (0.2-0.6 V/NHE). The mass transfer–corrected Tafel plots was deduced for the RDE analysis on Pt/CeO_2 NT electrocatalyst. The Tafel slope at a high current density had a value of 120 mV dec^{-1}, as expected for a first electron transfer rate determining step. Thanks for financial support: SECITI agreement ICYTDF/193/2012 and SIP-IPN under project MULTI-1611 2014 (Dengsong Zhang et al Journal of Solid State Chemistry 180 (2007) 654-660).

s6-013

Dependence of Pt-Nb_2O_5/C catalysts activity on the conditions of preparation of primary Nb_2O_5/C composites

Virginija Kepenienė, Jūratė Vaičiūnienė, Rokas Kondrotas, Vidas Pakštas, Loreta Tamašauskaitė-Tamašiūnaitė, E. Norkus
Center for Physical Sciences and Technology
A.Goštauto 9, LT-01108 Vilnius, Lithuania
virginalisk@gmail.com

Direct ethanol fuel cells (DEMFCs) have emerged as one of the most promising power sources for portable electronic devices, and electric vehicles by converting chemical energy directly into electrical energy in an environmentally friendly manner. Search for anode catalysts with improved catalytic properties for direct oxidation of ethanol in an alkaline medium has still been in progress.

In the present work, the primary Nb_2O_5/C composite was prepared in three different ways: (A) by mixing of dry Nb_2O_5 powder with graphite, Nb_2O_5:C ratio being 1:1, (B) by dispersion of Nb_2O_5 and graphite in a 2-propanol solution by ultrasonication for 30 min. with further dessication of the mixture and (C) by heating the Nb_2O_5:C composite obtained according to the procedure (B) at 500°C for 2h. Then Pt nanoparticles were dispersed over Nb_2O_5/C composites by the rapid microwave heating method. The surface morphology, structure and composition of the synthesized catalysts were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD) and inductively coupled optical emission spectroscopy (ICP-OES). The electrocatalytic activity of the synthesized catalysts towards the oxidation of ethanol in an alkaline medium was investigated by means of cyclic voltammetry and chronoamperometry.

It has been found that the Nb_2O_5/C catalyst modified with Pt nanoparticles enhance the ethanol oxidation current densities up to ca. 6 times, the mass activities for ethanol oxidation up to ca. 8 times and the specific activities for ethanol oxidation up to ca. 4 times as compared to those of graphite supported bare Pt catalyst.

Acknowledgement

Postdoctoral fellowship is being funded by European Union Structural Funds project ”Postdoctoral Fellowship Implementation in Lithuania”.

s6-014

Characterization of Cu_2ZnSnS_4 nanocrystal thin films for solar cells

Saghar (Sara) Khoshmashrab, Zhifeng Ding*
Department of Chemistry, The University of Western Ontario
1151 Richmond Street, London ON, N6A 5B7
skhoshma@uwo.ca

Solar cells have become one of the most promising sources of renewable energy. However, one of the most challenging tasks has been the development of cost-effective, non-toxic, efficient devices via a low energy and waste procedural method. Therefore, present work has focused on addressing these challenges by synthesizing Cu_2ZnSnS_4 (CZTS) light absorbing layers via a solvothermal, one-pot drop cast method. CZTS is an abundant, non-toxic quaternary semiconductor. It has a high absorption coefficient (10^4 cm^2) and a direct energy band gap of ~1.5 eV *(1)*; which is in alignment with the solar spectrum.

Photoelectrochemical (PEC) measurements and UV-Vis spectroscopy were used to evaluate the photovoltaic response and band gap (1.53 eV) of these films.

The photoresponse of CZTS nanocrystals was found to depend on the compositional ratio of the elements of the kesterite crystal structure (Fig. 1). An excess of sulfur and a 1.5:1:1.2 precursor molar ratio of CZTS was discovered to be the optimal.

The present work has also focused on the use of x-ray fluorescence (XRF), a non-destructive quantitative method, to measure the stoichiometric composition of these nanocrystals prior to and post drop cast.

The above characterizations have demonstrated to be efficient for successful fabrication of the CZTS films for solar cells.

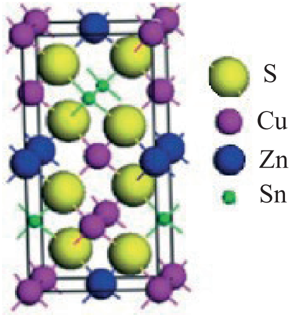


Figure 1. Kesterite structure of CZTS *(1)*.

Reference

1. Zhou, H.; Hsu, W-C.; Duan, H-S.; Bob, B.; Yang, W.; Song, T-B.; Hsu, C-J.; Yang, Y. CZTS nanocrystals: a promising approach for next generation thin film photovoltaics. *Energy Environ. Sci*. **2013**, *6*, 2822–2838.

s6-015

Synthesis and Electrochemical Study of Nanostructured PEDOT/MnO_2 Composites for Supercapacitor Applications

V.V.Kondratiev, A.O.Nizhegorodova, S.N.Eliseeva
Department of Chemistry, St. Petersburg University
Russian Federation, 198504, St-Petersburg, Petrodvoretz, Universitetsky pr.26
e-mail: vkondratiev@mail.ru

Transition metal oxides nanoparticles dispersed in conducting polymer matrices are promising materials for electrochemical supercapacitors due to their capability to provide high specific capacitance from combination of both constituents. In particular, the manganese oxide in combination with poly-3,4-ethylenedioxithiophene (PEDOT) has attracted interest as low-cost material with high specific capacitance and reversible charge-discharge processes providing the competitive parameters for supercapacitors.

In the present work, a simple cost-effective method of synthesis of composite PEDOT/MnO_2 with layered or uniformly dispersed manganese oxide particles has been adopted. The unique morphology of highly dispersed manganese oxide on PEDOT surface were characterized by STM and TEM. XPS spectroscopy was employed for identification of valence states of manganese in composites at different oxidation states.

Electrochemical properties of composites, obtained with variation of synthesis conditions, were investigated using cyclic voltammetry and constant current charging-discharging method and electrochemical impedance spectroscopy. The enhanced capacitive properties of composites can be mainly attributed to 3-D distribution of disperse MnO_2 into the mesoporous/macroporous structure of PEDOT with high surface area. The presence of conducting porous matrix facilitates ion diffusion and electron transfer, leads to the lowering the internal resistance of composite material and improves the electrochemical utilization of manganese oxide. The high stability of composite materials was shown by means of long-term cycling, where the low reduction in capacitance values was observed. The capacitive parameters of composites with different ratio between PEDOT and MnO_2 layers were systematically investigated and analyzed.

Financial support from Saint Petersburg State University (grant №12.38.15.2011) and Russian Foundation for Basic Research (grant №13-03-00894) is gratefully acknowledged.

s6-016

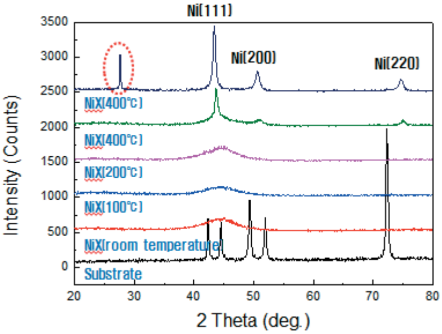
Fabrication of Micro Probe Pin through Electrolytic and Electroless Ni Alloy Deposition

Joo-Yul Lee, Yongsoo Jeong
Korea Institute of Materials Science
797 Changwondaero, Seongsangu, Changwon, Gyeongnam, 642-831, Korea
leeact@kims.re.kr

Micro probe pin is a critical component of probe card system assessing the electrical performance of individual memory chips and system IC which are fabricated using sophisticated MEMS (microelectro-mechanical systems) techniques. This probe pin can be manufactured effectively and economically by combining electrolytic and electroless deposition techniques, which are able to control surface properties such and three dimensional morphology and mechanical characteristics on the silicone mold .

We manufactured silicon wafer molded after the shape of micro probe pin array using wet etching process frequently used in the semiconductor manufacturing process. Thin copper seed layer was formed on top of entire silicon wafer front surface, and nickel alloy layer of 10 um thick was electrolessly deposited. Then, nickel-cobalt alloy electrodeposition and chemical mechanical polishing were done successively to get specified and uniform micro pin array. All micro probe pins were annealed in the N_2/H_2 environment at 400°C for one hour to get hard surface property above Hv. 700 which is acceptable microhardness level standing at repetitive touchdown test over 500,000 times.

We observed the effect of reducing agent, DMAB, solution acidity and solution temperature on the electroless Ni alloy deposition process. We performed a series of linear sweep voltammetry and measured the rate of thin Ni alloy deposition at different plating parameters.



[Fig.1] XRD data of Ni alloys at different annealing temperature

s6-017

Synthesis of N, Zr Co-doped Mesoporous TiO_2 with Enhanced Photocurrent and Photocatalytic Activity

Haijin Liu[1, 2], Guosheng Wu[1], Sapanbir Thind[1], Jiali Wen[1] Aicheng Chen*[1]
1. *Department of Chemistry, Lakehead University, 955 Oliver Road, Thunder Bay, ON P7B 5E1, Canada*
2. *School of Environmental Science, Henan Normal University, , Xinxiang 453007, PR China*
achen@lakeheadu.ca

Titanium dioxide (TiO_2) has been widely used in photocatalysis, hydrogen production, self-cleaning materials, fuel cells and myriad other fields [1-3]. Although TiO_2 has been considered as the most promising semiconductor in many fields, the well-known drawbacks of wide band gap and high recombination rate of electron-hole pairs restrict its applications. Some metal and non-metal doping into TiO_2 can narrow the band gap of TiO_2 and arouse visible light response.

In this study, we synthesized N, Zr co-doped TiO_2 using a facile combustion method and investigated their photoelectrochemical properties as well as photocatalytic activities both under simulated sunlight and visible light irradiation. The fabricated N, Zr co-doped TiO_2nanoparticles were characterized by transmission electron microscopy, Brunauer–Emmett–Teller (BET) surface area analyzer, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-Visible reflectance spectroscopy. Furthermore, linear voltammogram (LV) and Chronoamperometry (CA) were carried out to measure their photoelectrochemical responses. Our studies have shown that the band gap energy of as-synthesized N, Zr co-doped TiO_2 was between 2.71 to 2.76 eV. Among all the N, Zr co-doped TiO_2 samples, the electrode with 1.0% Zr doping exhibited the highest photocurrent under visible light and simulated solar light.

References:

[1] S. S. Thind, G. Wu, A. Chen, *Appl. Catal. B* 111(2012) 38-45.
[2] S. S. Thind, G. Wu, M. Tian, A. Chen, *Nanotechnology* 23 (2012) 475706.
[3] H. Liu, G. Liu, X. Shi. *Colloids Surf.* A 363 (2011) 35-40.

s6-018

Anodic Dissolution of Vapor Deposited Nickel: Investigation of Residue Formation

Andrew Morrison, Golam Moula, Jacek Lipkowski
University of Guelph
50 Stone Road East, Guelph, Ont., N1G2W1
amorri03@uoguelph.ca

The anodic dissolution of vapor deposition nickel is an important process. Used in the electroplating industry to plate automotive parts, this process provides corrosion resistance to external conditions. This is possible due to nickel's unique property of self-passivation, where a thin oxide film forms over the nickel metal creating a very resistive nickel oxide layer which is not easily removed when interaction with oxygen occurs.

Issues arise in the electroplating process due to buildup of nickel oxide and nickel metal residues within the reaction chamber which causes voltage leakage along with shut downs to clean and remove the residues. This leads to increased costs for companies. Many ideas have been investigated into the causes of this residue build –up. This project focuses on the conditions for growth of the nickel pellets and chips used for the electroplating process. These pellets are grown using the Mond Process which purifies the nickel by flowing CO over the impure nickel creating nickel carbonyl ($Ni(CO)_{4(g)}$). This nickel carbonyl gas is then sent into a reaction chamber where "seed" nickel pellets are used to grow these pellets layer by layer from ~1 mm to ~10 mm in diameter.

In order to determine if the growing conditions are the reason for the increased residue formations laboratory-grown samples were produced with different temperature and vapor deposition nickel gas concentrations. These samples contain different layers which were grown at specific temperatures and gas concentrations to determine corrosion rate. These lab grown samples, provided by Vale Canada, are then anodically dissolved at 60ºC, using 0.8 A/dm^2 in 10 minute intervals in order to observe the progression of the dissolution. In order to observe the surface changes after the dissolution Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and White Light Interference Microscopy (WLIM) are used to characterize the surfaces. Determining the surface roughness, average grain size, and grain distribution will lead to a better understanding of how the samples dissolve during the dissolution and determine which conditions lead to increased residue formations.

s6-019

Relation Between the Electrochemical Dissolution and Surface Morphology of Vapor Deposited Nickel

M.G. Moula,[1] *H. Huang*[2] *and J. Lipkowski*[1,*]
[1]Dept. of Chemistry, Univ. of Guelph, 50 Stone Road East, Guelph, ON, N1G 2W1
[2] Vale Base Metals Tech. Develop., 2060 Flavelle Boulevard, Sheridan Park, Missi., ON, L5K 1Z9
*Corresponding author: jlipkows@uoguelph.ca

The dissolution behaviour of lab made vapour deposited nickel samples was studied successfully using different microscopic techniques. We have seen clear differences between the investigated samples. A large difference in the surface morphology was observed on sample A that consisted of smaller grains and narrower grain distribution [(Fig. 1(a) and (c)] and sample B that consisted of larger grains and broader grain distribution. Open pits formed on the surface A which grew laterally and finally merged but the depth of the pits remained constant suggesting layer by layer dissolution behavior. This observation suggests that this surface may produce fewer residues. In contrast, the sample B [Fig. (b) and (d)] did not show a drastic change of dissolution behavior like sample A after 20 minutes of dissolution. We observed open pits and closed pits on this surface. This surface is favorable for crevice corrosion due to the presence of small crystals around the large crystals. Small crystals dissolved faster which created small holes around the large crystals favouring crevice corrosion. This type of dissolution may result in more residue formation.

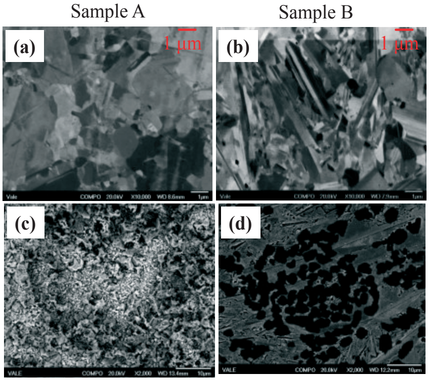


Figure1. Sample A: SEM images before (a) and after 120 minutes (c) of dissolution. Sample B: SEM images before (b) and after 120 minutes (d) of dissolution.

s6-020

Titanium Oxide-based Nanocrystalline Materials for Pseudocapacitors

Martin Opitz[1], J. F. Beleites[2], Junpei Yue[2], B. Smarsly[2], B.Roling[1]
[1]*Department of Chemistry, University of Marburg*
Hans-Meerwein-Straße, 35032 Marburg, Germany
[2]*Department of Chemistry, University of Gießen*
Heinrich-Buff-Ring 58, 35392 Gießen
martin.opitz@chemie.uni-marburg.de

In recent years, pseudocapacitive charge storage systems have gained a lot of interest. In particular, ruthenium and manganese oxides were studied with respect to their application in pseudocapacitors.[1]

Cheaper alternative materials are titanium oxides. Recent studies have shown that in nanocrystalline titanium oxides, a transition from Faradaic lithium storage to capacitive lithium storage takes place, when the particle size is reduced.[2] Motivated by this finding, we prepared thin films of nanocrystalline titanium oxides and carried out electrochemical tests by means of cyclic voltammetry and impedance spectroscopy. We discuss the relation between structural, electronic and electrochemical properties.

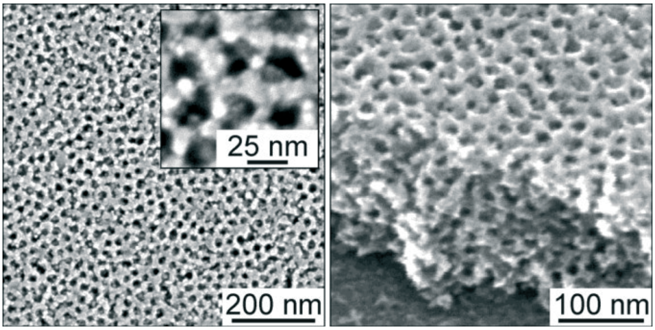


Figure: Scanning electron microscopy picture of titanium oxide-based thin layers. Left: top view, right side-face of an crosssection.[3]

---

[1] P. Simon, Y. Gogotsi, *Nat Mat* **2008**, *7*, 845.

[2] J. Wang, J. Polleux, J. Lim, B. Dunn, *J. Phys. Chem. C* **2007**, *111*, 14925.

[3] Dr. T. Brezesinski, Karlsruhe Institute of Technology, Ocotber 2011.

s6-021

Characterization and Modification of Surface Topography During Electrodeposition of Tin and Zinc Based Alloys from Citrate Complex Baths

Piotr Ozga, Honorata Kazimierczak, Monika Słupska
Polish Academy of Sciences, Institute of Metallurgy and Materials Science
30-059 Kraków (Cracow), 25 Reymonta St., Poland
p.ozga@imim.pl

Tin-zinc and tin-manganese alloys are especially interesting as the replacement materials for toxic cadmium layers and coatings with Cr(VI)-based conversion layer (high corrosive resistance). Both systems combine the barrier properties of tin with the barrier and the sacrificial protection afforded by zinc or manganese. The presence of molybdenum or tungsten in ternary alloys plays similar role to presence of chromium(VI). In case of tin, the columnar type of structures with large grains are characteristic for tin electrodeposits from solutions contained simple hydrated ions of tin(II). Electrodeposition of tin and tin alloys from complex solutions, as for example from citrate solutions changes type of structure to fine grained. Additional refinement of structure and changes of the crystallographic preferred orientation are the results of the presence of molybdenum(VI) and tungsten(VI) complex species in citrate solution for deposition of ternary alloys: tin-zinc and tin-manganese with molybdenum and tungsten. We also investigated modification of surface topography by addition of surfactant - PEG (polyethylene glycol) to bath. The additives of PEG with different chain length i.e. average molecular weight from 1500 to 20000 was investigated in the range of concentrations from 0.1 to 2 g/dm^3. The surface topography was investigated by atomic force microscopy (AFM). The roughness parameters : roughness average (Sa), surface skewness (Ssk) and surface kurtosis (Sku) were determined for metal and alloys coatings with different thickness from 0.2 μm to 10 μm. The advanced roughness analysis using Ssk-Sku diagrams enables on the more detailed analysis of the characteristics of changes of surface topography with thickness of the layer, concentration of surfactant as also surfactant properties. Such experimental diagrams lead to the efficient finding of optimum conditions for obtaining the deposits with the best properties of deposit surface for some application (as for example: bright, satin bright, matte and etc). They also help to determine the model of growth mechanisms of deposit as also range of parameters of electrolytic bath and electrolysis with is the most desirable growth of layer.

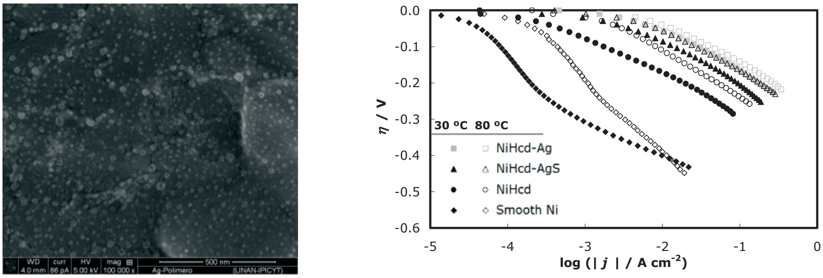
Acknowledgements : This work was supported by project : POIG-01.01.02-00-015/09-00.

s6-022

Activation of Macroporous Ni electrodes with Ag and AgS Nanoparticles for Hydrogen Production

C. González-Buch[1], E.M. Ortega[1], G. González[2], I. Pedre[2] M. G. Sánchez-Loredo[3]
V. Pérez-Herranz[1*]
[1]IEC Group, Depto. Ingeniería Química y Nuclear, Universitat Politècnica de València. Camí de Vera, s/n. 46022 Valencia, Spain. [2]INQUIMAE, Facultad de Ciencias Exactas y Naturales,Universidad de Buenos Aires, Consejo Nacional de Investigaciones Cientficas y Técnicas, (1428) Buenos Aires, Argentina. [3]Instituto de Metalurgia/Facultad de Ingeniera, Universidad Autónoma de San Luis Potosí, Sierra Leona 550, 78210, SLP - México
**vperez@iqn.upv.es*

The main goal of modern electrocatalysis for the hydrogen evolution reaction (HER) is to enhance the activity of the electrodes whit less usage of noble metals. Supporting materials with high surface area are essential to reduce the dosage of metal loading. Considering the above facts, in this work, macroporous electrodes have been synthesized by galvanostatic electrodeposition at high current density [1] and then, they were modified with silver nanoparticles (AgNps). The AgNps were synthesized using polivinylpyrrolidone as the stabilizing agent. The anoparticle dispersion was suspended in a polymer solution containing polyallylamine and sodium dodecylsulfate (see Fig.1a) [2], and this mixture was deposited on the developed macroporous electrodes. The HER activity of these electrodes was studied in 30% wt. KOH by means pseudo-steady-state polarization curves and electrochemical impedance spectroscopy (EIS). As it can be seen in Fig. 1b, Nps modified electrodes show higher catalytic activity than the NiHcd electrode and than a commercial smooth Ni electrode.



(a) (b)

Fig 1. (a) FEG-SEM image of PVP-capped silver nanoparticles dispersed in the polymeric matrix**. (b)** Linear Tafel polarization curves recorded on the investigated electrocatalytic coatings in 30 wt.% KOH solution at 30 and 80 ºC

[1] C.A. Marozzi, A.C. Chialvo, Electrochim Acta 45 (2000) 2111.
[2] M.L. Cortéz, G.A. González, F. Battaglini, Electroanal 23 (2011) 156.

s6-023

The ab-initio study of iron phtalocyanie derived Fe-SPc catalysts for oxygen reduction reaction (ORR) in PEM Fuel Cells

Min Ho Seo[a], Hey Woong park[a], Drew Higgins[a], and Zhongwei Chen[a]*
[a]*Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, ON, N2L 3G1, Canada*
e-mail address: zhwchen@uwaterloo.ca

Pt remains as the only metal that is currently used as an electrocatalyst in acid-based proton exchange membrane fuel cells (PEMFCs) owing to its ability to function under such harsh conditions. Unfortunately, most of the active catalysts, such as Ni, Co or Cu, are thermodynamically or electrochemically unstable at low pH and/or high potentials in the context of electrocatalytic reactions involving H_2 or O_2 species[1-3]. Accordingly, considerable attention has been focused on reducing the amount of Pt in real-world applications, especially for cathodes that employ a high loading of Pt. However, several approaches recently have been attempted to not only decrease the Pt content in fuel cell electrocatalysts but also to replace it with less expensive materials[4-9]. Among the non-precious metals, transition metal macrocycle compounds opened a new direction for the research in the field, leading to numerous investigations in ORR electrocatalyst materials. However, the understanding of the activity and durability are quiet difficult due to uncertainties in electronic structure changes and bond strength of active site and the oxygen. Even, the performance of the catalyst is severely changed before/after pyrolysis of transition metal macrocycle compounds. Therefore, The importance of the research in the non-pyrolyzed macrocycle compounds is emphasized as initial study. This work is carried out to understand the activity and durability of the Iron phthalocyanine (Fe-Pc) and Ferrous 2,9,16,23-tetra-(2′,6′-diphenylphenthioether)phthalocyanine (Fe-SPc) catalyst (see Fig. 1) through the ab-initio computational method and experimental analyses.

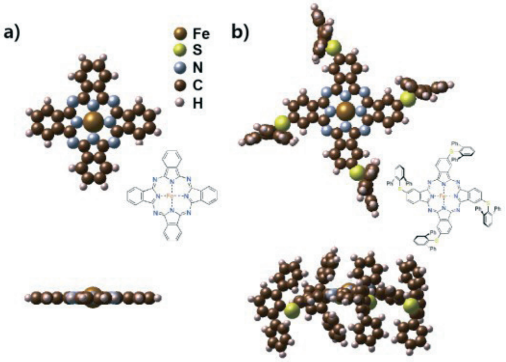


Fig. 1 the top and side view of (a) FePc and (b) FeSPc after relaxation

s6-024

Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy Investigations of Thiosulfate Gold Leaching

Scott. R. Smith[a], Song-Bo Li[b], Xiang-Dong Tian[b], Yi-Fan Huang[b], Zhong-Qun Tian[b], Janet Y. Baron[c], Yeonuk Choi[c], Jacek Lipkowski[a]
[a] Department of Chemistry, University of Guelph, Guelph, ON, N1G 2W1, Canada
[b] State Key Laboratory of Physical Chemistry of Solid Surfaces and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fuijan, China
[c] Barrick Gold Corporation, Toronto, ON, M5J 2S1, CANADA
Presenting author: ssmith42@uoguelph.ca

Recent studies of the Au leaching process have employed thiosulfate as the alternative complexing ligand to cyanide for gold extraction from ores containing carbonaceous components which preferentially absorbs gold and gold-cyanide complexes (the so called *preg-robbing ores*). Thiosulfate, in the presence of an appropriate oxidant such as dissolved oxygen, is well known to complex Au(I) ions and form a soluble $[Au(S_2O_3)_2]^{3-}$ complex. However, the kinetics of this process are inhibited by the formation of a passivating layer of species on the Au surface that block the lixiviant reagents from reaching the underlying Au atoms, thereby preventing full recovery of Au from the ore. To determine the composition of this passive layer, the interfacial behaviour of nanostructured Au electrode upon immersion into a thiosulfate electrolyte solution was investigated using surface enhanced Raman spectroscopy (SERS). The high kinetic rate of Au dissolution by thiosulfate results in continual loss of unprotected nanostructured features designed for optimal surface enhancement. Therefore, changes or variations in observed spectral features are highly convoluted with changes in surface enhancement. In an attempt to circumvent or mitigate these effects, Au electrodes have been designed with arrays shell-isolated nanoparticles and will be compared and contrasted in terms of their applicability for studying the Au leaching system with SERS. Raman bands indicative of adsorbed tetrathionate, trithionate, and $[Au(S_2O_3)_2]^{3-}$ were identified at early immersion times. However, characterization of changes in the spectral features suggest that complexation of the oxidized Au atoms by thiosulfate and its subsequent mass transportation into the bulk electrolyte is the predominantly favoured pathway at early immersion times. However, the disappearance of the Raman bands characteristic of the $[Au(S_2O_3)_2]^{3-}$ complex and the appearance of bands indicative of elemental sulfur on the Au surface at longer immersion times confirms the growth of a passivating film of elemental sulfur on the gold surface in the thiosulfate electrolyte, albeit at much longer immersion times.

s6-025

Localized Investigations of the Electrochemical Properties of Lithium Iron Phosphate Films using Micro-Pipets

M.E. Snowden,[1,2] S. Gervais,[2] S.B. Schougaard,[2] J. Mauzeroll[1]
1, McGill University 2, Université du Québec à Montréal
McGill University,
Department of Chemistry,
801 Sherbrooke Street West,
Montreal, Canada, H3A 0B8
Michael.Snowden@mail.mcgill.ca

Lithium ion batteries are a commercially successful method of providing portable electrical energy, demonstrated by their mass market use in portable electronics and growing interest as an alternative power source within the automotive industry.[1] For the lithium ion battery to rival fossil fuels as an automotive energy source, lithium ion batteries need to have improved capacity and charge/discharge rates. As new anode and cathode materials are developed[2] they are typically screened for advantageous properties by assembly into a working battery. This involves the fabrication of a film from a mixture of conductive material (*e.g*. carbon), a binder (*e.g*. polyvinylidene fluoride), and the active material of interest. The mixture is then cast onto a conductive material to form a thin film, before assembly within a coin cell. How the film is prepared, the ratio of the individual components of the film and the final assembly of the coin cell can significantly alter the performance of the battery.[3,4] This could give misleading information about the effectiveness of a novel active material.

Here we present proof of principle measurements to demonstrate the suitability of micro-pipet measurements for probing lithium ion battery materials. Specifically, we probed lithium iron phosphate films to determine the working potentials of the film, and the charge capacity of the material. Lithium iron phosphate was a convenient test material, which provided stability under atmospheric conditions and was compatible with water. Data obtained on candidate films by micro-pipet measurements were compared to coin cell measurements, highlighting the suitability of this technique for future investigations of lithium ion battery materials.

1) Wagner, F. T.; Lakshmanan, B.; Mathias, M. F.; *J. Phys. Chem. Lett.*, **2010**, *1* (14), 2204–2219
2) Whittingham, M.S.; *Chem. Rev.*, **2004**, *104* (10), 4271–4302
3) Bruce, P. G.; Scrosati, B.; Tarascon, J.-M.; *Angew. Chem.-Int. Ed.* **2008**, *47*

s6-026

Comparative exploration of the surface electrochemistry of Ir-IrO_2 (111 / 110) and Ru-RuO_2 (0001) single crystal model catalysts for the oxygen evolution reaction (OER)

Camillo Spöri[1,2], David P. Wilkinson[2], Peter Strasser[1]
[1]Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany
The Electrochemical Catalysis, Energy and Materials Lab
[2]University of British Columbia, 2360 East Mall, Vancouver BC V6T 1Z3, Canada
Department of Chemical and Biological Engineering
camillo.spoeri@tu-berlin.de

Overcoming the current drawbacks of the oxygen evolution reaction (OER) plays a major role for establishing electrocatalytic water splitting as main pathway in sustainable hydrogen production [1]. The latter is considered a key requirement to establish a hydrogen economy [2]. Secondary, the OER is a major side-reaction in many other technical electrolysis processes such as chlorine evolution [3]. A better understanding of the underlying mechanism of oxygen evolution is substantial to design new catalysts with higher efficiency and stability together with lower costs.

In order to elucidate the influence of steps, kinks and edges of nanoparticularly shaped catalysts, different single crystal surfaces of the to this date best known OER catalysts are investigated.

We present an improved inductive electrochemical cell, derived from [4], which allows standard pressure temperature treatment and direct electrochemical characterization of metal electrodes within the same cell. To the best of our knowledge this system has not been applied to OER catalysts so far. Pristine iridium and ruthenium single crystals are prepared by inductive heating in reducing gas atmospheres such as CO and H_2. Surface oxidation processes are observed and the electrocatalytic activities of the metal surfaces after different oxidation procedures are compared with the pristine surfaces. Influences of the surface plane and the employed elements are highlighted and interpreted.

[1] Holger Dau, Christian Limberg, Tobias Reier, Marcel Risch, Stefan Roggan, P. Strasser, ChemCatChem, 2 (2010) 724-761.

[2] Marcelo Carmo, David L. Fritz, Jürgen Mergel, D. Stolten, International Journal of Hydrogen Energy, 38 (2013) 4901-4934.

[3] Valery Petrykin, Katerina Macounova, Jiri Franc, Oleg Shlyakhtin, Mariana Klementova, Sanjeev Mukerjee, P. Krtil, Chemistry of Materials, 23 (2011) 200-207.

[4] Alexander S. Bondarenko, Ifan E.L. Stephens, I. Chorkendorff, Electrochemistry Communications, 23 (2012) 33-36.

s6-027

Selenization of $CuInS_2$ Nanocrystal Films: Controlling Dropcasting Uniformity by Post-Synthesis Addition of PVP

Daniel L. Stitt, Zhifeng Ding*
Department of Chemistry, The University of Western Ontario
1151 Richmond Street, London, Ontario, Canada, N6A 5B7
dstitt@uwo.ca

Copper Indium Disuflide ($CuInS_2$, CIS) is a p-type semiconductor that has shown promise as a light-absorbing layer due to relatively high photovoltaic efficiency, tunable band gap and air stability. A one-pot solvothermal method for production of CIS nanonocrystals has previously been developed by the Ding group[1]. Deposition of CIS nanocrystals onto a conductive substrate is required to produce photovoltaic devices. However methods of producing a uniform layer is often difficult and expensive. The simplest and cheapest method of deposition requires placing a dispersion of nanocrystals within a volatile and polar solvent onto the subsrate surface. This dropcasting method however, often shows non-uniformity, cracks, and pores which negatively effect the efficiency of photocurrent production. Polyvinylpyrrolidone (PVP) is a polymer well known for its solubility in polar protic solvents. PVP finds use as a capping agent in nanocrystal synthesis and can be used to decrease particle size. Dispersion of CIS nanocrystals in a solution containing PVP decreased particle size resulting in a more uniform layer. Addition of PVP however, lowered the efficiency of CIS deposits in photovoltaic devices due to a decreased ratio of CIS in the deposit. By annealing CIS deposited with PVP in a selenium atmosphere, PVP was decomposed while loss of sulfur was compensated by incorporation of selenium into the CIS crystal structure resulting in a uniform layer of photosensitive CI(S,Se). Characterization of the developed layer was carried out using electrochemical techniques including linear voltammetery of a photoelectrochemical cell using a methyl viologen solution as a pseudo-n-junction and a xenon light source with alternating on/off conditions. Other characterization methods have been employed. including x-ray fluorescence (XRF) and scanning electron microscopy (SEM).

[1] A. Tapley, D. Vaccarello, J. Hedges, F. Jia, D. A. Love, Z. Ding, Preparation and characterization of $CuInS_2$ nanocrystals for photovoltaic materials, Phys. Chem. Chem. Phys. 15 (2013) 1431.

s6-028

Decomposition Aluminate solutions from the Electrochemical reaction with Metallic aluminum

Suleimenov E.N
Kazakh British Technical University
Tole by str 59, of 219   Almaty, 050 000
Republic of Kazakhastan
e-mail metallaim@mail.ru

In studies of the electrical conductivity and resistance aluminate solution has been shown that the frequency of the electrical current has a significant impact on the conductivity of the electrical conductivity of solutions.

These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated. Investigated the effect of current frequency , current, and temperature on the electrical conductivity of aluminate solutions (Na_2O 250 g / l and caustic module k = 1,7). We used two-electrode cell volume of 100 ml with platinum electrodes . The solution temperature was varied from 25 to 700C . It is established that an increase in current strength of 1 to 500 mA the resistance of the solution is reduced from 36 to 9,5 Ohm, the dependence is extreme. Dependence of the resistance on the concentration of the solution at low frequencies of electrical current is also extreme. It is shown that the aluminate solution "remembers" changes in electrical resistance readings. When a current is passed for a longer time (60 - 120 min), the resistance reading stabilized. After stress relief after some time the solution had acquired a resistance equal to the initial indications. These data suggest the molecular structure of aluminate solutions that formed the basis for developing a method of decomposition of aluminate solutions using alternating electric current.

In studies of the solubility of metals in aqueous solutions of inorganic been found that transient electric current causes dissolution of metal, which with conventional methods do not go into solution. Transition of metallic aluminum in aluminate solution causes rapid structural stability violation aluminate solution. Therefore, studies were conducted on the decomposition of the aluminate solution by electrochemical dissolution reaction of aluminum in the solution.

Decomposition of chemically resistant aluminate solutions was carried out in a two-electrode cell at a frequency of 20 and 50 Hz. Amperage was varied from 150 to 300 MA. After processing, the solution was decomposed electric current for 12 hours to extract the precipitate of aluminum and up to 75% higher. According to the literature, industrial aluminate solutions decompose spontaneously within three years with the same parameters as the data for the current frequency of 20 Hz.

s6-029

Characterization and Optimization of $CuInS_2$ as a light absorbing layer for Solar Cells

A Tapley[a], D.A. Love[b], Z. Ding[a]
[a] *Department of Chemistry, Western University*
1151 Richmond Street, London Ontario, N6A 5B7
[b] *Rosstech Inc,*
71 15th Line South, Orillia, ON
zfding@uwo.ca

The need for an inexpensive, reliable and an environmentally safe source of energy increases every year. Solar energy has the potential to meet the energy needs of modern society if the technology can be developed to compete with cheaper energy sources. $CuInS_2$ (CIS) is a light absorbing p-type semiconductor that shows a lot of potential to reduce the costs of harnessing solar energy. It has a direct band gap of around 1.4 to 1.5 eV and a high absorption coefficient making it an ideal candidate for the absorbing layer in thin film based solar cells.[1] Current methodologies of synthesizing CIS often involve high temperatures and a hydrogen sulfide atmosphere.[2] These expensive and dangerous processes are preventing CIS from being commercialized. The following work investigates a one-pot synthesis of CIS nanocrystals (NCs) that uses relatively low temperatures and has no need of a hydrogen sulfide atmosphere.[3] Photoelectrochemical measurements were used to investigate not only the quantity of photocurrent the CIS NCs produced but as well as the relative quality. Band gap studies using various techniques were carried out as a comparative study.

CIS as a monolayer was also investigated. The fluorine doped indium oxide substrate was functionalized with a linker molecule that has the potential to associate with the CIS and chemically attach the NCs to the surface. The monolayer formed was probed using similar methods as the drop cast layer.

The two different methods of deposition and the vast amount of characterization performed on both will give insight into what specifically makes quality CIS layer so that when it is incorporated into a full device the highest efficiency possible will be obtained.

[1] J. Xu, Y. Wang, Materials Letters, 99 (2013) 90-93.
[2] W. Liu, D.B. Mitzi, M. Yuan, A.J. Kellock, S.J. Chey, O. Gunawan, Chemistry of Materials, 22 (2010) 1010-1014.
[3] A. Tapley, D. Vaccarello, J. Hedges, F. Jia, D.A. Love, Z. Ding, Physical Chemistry Chemical Physics, (2013) 1431-1436

s6-030

Electrochemical behavior of Tau protein domain on binding to aggregation agent

Hanna Trzeciakiewicz, Sanela Martic
Oakland University, Department of Chemistry
2200 N. Squirrel Road
Rochester, MI 48309-4401
htrzecia@oakland.edu
martic@oakland.edu

Tau is a non-catalytic structural protein most commonly found in neurons, that promotes tubulin assembly and stabilizes axonal microtubules at various domains of the protein. Tau aggregates into soluble oligomers, paired helical filaments, and neurofibrillary tangles, which are hallmark biomarkers for neurodegenerative diseases such as Alzheimer disease and dementia. To understand the early-onset of aggregation of Tau protein, we carried out in vitro electrochemical studies in the presence of inducing agents such as heparin and arachidonic acid, which promote Tau aggregation, as a model system. The electrochemical methods used were Electrochemical Impedance Spectroscopy and Cyclic Voltammetry. This approach allowed us to probe the effect of Tau domain on the biomolecular interactions and which domains are key in the early stages of aggregation. Then by finding the optimal domains, we monitored which agent promotes Tau aggregation by observing the formation of Tau-agent complex, Tau-Agent-Tau complex and Tau dimer. Our findings suggested that agent binding to the Tau proteins is domain specific. The effects of concentration, temperature, time, and pH with respect to the aggregation agent binding to Tau protein will be presented.

s6-031

PECM Study of Post-Synthesis PVP Addition and Selenization as a Method for Improving CZTS Films

Matthew J. Turnbull, Zhifeng Ding*
The Department of Chemistry Western University
1151 Richmond Street, London Ontario, N6A 5B7
zfding@uwo.ca

With an ever growing population, the world is seeking new sources for low-cost, renewable energy.[1] Cu_2ZnSnS_4 (CZTS) nanocrystals (NCs) are made of earth abundant elements with a band gap of 1.45-1.51 eV.[1] This p-type semiconductor is of great interest for its uses in second generation solar cell devices.[1] The deposition of a thin film of this photoabsorbing layer has long been shown to contain microscale imperfections, grooves, and holes. These imperfections impede the flow of electrons, ultimately reducing the photocurrent in solar cells. The use of polyvinylpyrrolidone (PVP) as a post-synthesis additive was investigated as a method for reducing these imperfections and packing the NCs into a tighter film. The addition of PVP increases the polarity and results in firmly packed films, but restricts the flow of electrons through the semiconductor, causing poor photoresponse. Restoration of the photoresponse required the removal of PVP, which was expected to be possible at high temperatures using thermogravimetric analysis (TGA). Annealing in a selenium atmosphere was shown to reduce film imperfections[2], and was coupled to PVP removal. The CZTS NCs were synthesized in a one-pot solvothermal process. Post workup addition of PVP to CZTS in isopropanol was studied in dropcast films on fluorine doped tin oxide (FTO) glass, molybdenum coated glass, and pre-annealed glass of both varieties. Samples were then annealed at 500^0C in a selenium atmosphere to restore the photocurrent and remove PVP, and the resultant films studied using photoelectrochemical measurements (PECMs). PECMs allow us to quantify the photoresponse by the current density associated with these layers without completing an entire solar cell device.[3]

[1] D. Vaccarello, A. Tapley, Ding, Z, Optimization of the Cu_2ZnSnS_4 Nanocrystal Recipe by Means of Photoelectrochemical Measurements, R. Soc. Chem. Adv. 3 (2013) 3512.
[2] Guo, Q.; Hillhouse, H. W.; Agrawal, R. Synthesis of Cu_2ZnSnS_4 Nanocrystal Ink and Its Use for Solar Cells. J. Am. Chem. Soc. 131 (2009) 11672-11673.
[3] H. Ye, H. Park, V. Akhaven, B. Goodfellow, M. Panthani, B. Korgel, A. Bard, J. Phys. Chem. C. 115 (2011) 234-240.

s6-032

Fast and slow processes at the interface between ionic liquids and Au(111)-electrodes

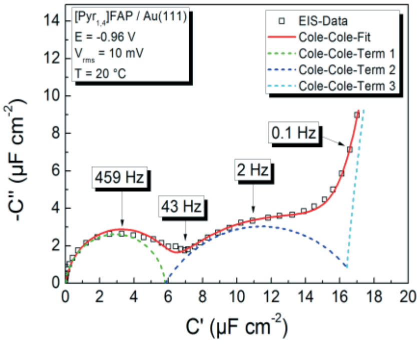
Jens Wallauer, Marcel Drüschler, Bernhard Roling
Department of Chemistry, Philipps-University Marburg
Hans-Meerwein Straße, D-35032Marburg, Germany
Jens.Wallauer@chemie.uni-marburg.de

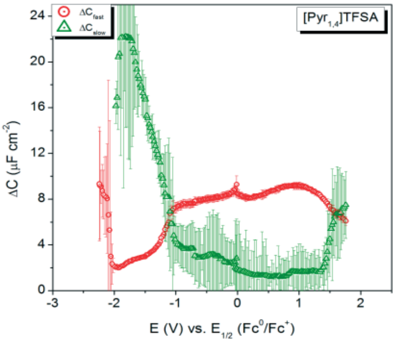
Many technological advances are based on capacitive or pseudo-capacitive processes in the interfacial region between an electrode and the electrolyte. These include storage of electrical energy in supercapacitors, double-layer field-effect transistors, or applications in material science like metal deposition. Due to their good ionic conductivities, broad electrochemical stability windows and low flammability, Room-Temperature Ionic Liquids (RTIL) show a great potential as electrolytes in these applications.

The differential double-layer capacitance describes the charge that is being stored in the electrochemical double-layer while changing the electrode potential. It is an important quantity in the description of the interfacial structure because it is strongly related to ion-ion or ion-electrode interactions.

The differential capacitance can be analyzed by electrochemical impedance spectroscopy (EIS). This method allows the evaluation of capacitive processes on different time scales. We found that not only the charging of the double-layer in the millisecond domain contributes to the overall differential capacitance but also slower processes with time scales of seconds or slower in certain potential regions. Possible causes of these slow processes include reconstruction of the gold surface or formation of ordered adsorbate layers of counter ions.

[1] M. Drüschler et al., *Phys. Chem. Chem. Phys.* **14** (2012) 5090-5099.
[2] J. Wallauer et al., *Z. Naturforsch.* **68b** (2013) 1143-1153.





s6-033

ElectroChemical Studies of Gold Leaching in Thiosulfate Solution with Copper

Chunqing Zhou[1], Scott Smith[1], Jacek Lipkowski[1], Yeonuk Choi[2]
[1]Department of Chemistry, University of Guelph
50 Stone Road East
Guelph, ON, Canada N1G 2W1
(chunqing@uoguelph.ca, jlipkows@uoguelph.ca)
[2]Barrick Gold Corporation
3700-161 Bay Street
Toronto, ON Canada M5J 2S1

Open-circuit potential tracking and polarization resistance measurements have been employed to study gold leaching in thiosulfate solution. It has shown that gold dissolution has been improved with the addition of Cu(II) into the leaching solution. It is observed that in the presence of the Cu(II)/Cu(I) redox couple gold leaching takes place at a higher open circuit potential (OCP) and that consequently gold dissolves faster in the presence of Cu(II) than in the copper free thiosulfate solution.

Poster presentation

s7-001

Electrochemical response from cylindrical nanopore electrode arrays

Mahdieh Atighilorestani and Alexandre G. Brolo
Department of Chemistry, University of Victoria, 3800 Finnerty Road, Victoria BC
V8P 5C2, Canada
E-mail: agbrolo@uvic.ca

Arrays of cylindrical nanopores on gold thin films, fabricated by either focused ion beam (FIB) or interference lithography (IL), can be used as nanoelectrodes. One of the advantages of these nanopores is that their electrochemical response can be synchronized with surface plasmon resonance (SPR), allowing simultaneous optical characterization of the electrochemical process at the nanoscale.

In this study, the current response of these cylindrical nanopore electrode arrays has been simulated using COMSOL Multiphysics® in three-dimensional domain. Simulation results showed that the current density at the cylindrical nanopore arrays is greater than the current density at recessed nanodisc arrays.

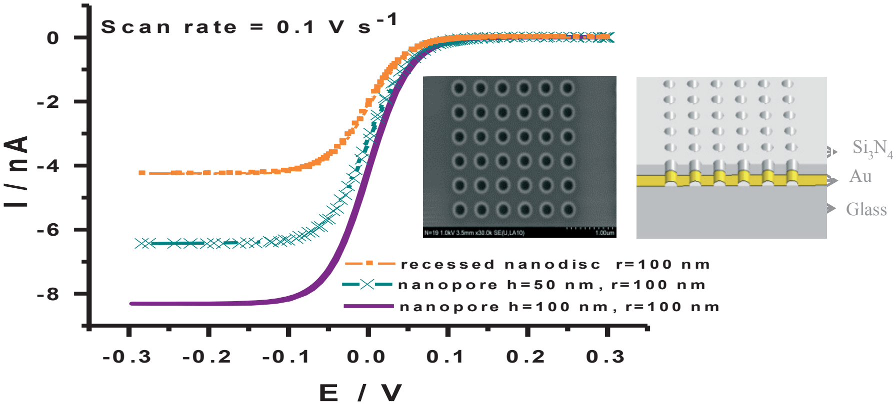


Figure: Comparison of cyclic voltammogram at a 6 ×6 recessed nanodiscs array and cyclic voltammograms at 6 ×6 cylindrical nanopore arrays of height 50 nm and 100 nm for different scan rates. The inserted SEM image shows a 6×6 cylindrical nanopores electrode array fabricated by FIB. And the cartoon represents the cross sectional area of an array of cylindrical nanopore electrodes.

s7-002

Electrocatalytic Activity of PtIr and PtRu Nanoparticles Deposited on TiO_2 Nanotubes

Walaa Alammari, Kevin Gagnon, Aicheng Chen
Department of Chemistry, Lakehead University
955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada
Wsalamma@lakeheadu.ca, achen@lakeheadu.ca

Direct Methanol Fuel Cell (DMFC) is a promising future energy technology alternative to conventional energy generating devices because of its high energy conversion efficiency, low-to-zero pollutant emission, methanol fuel availability, ease in distribution, and high energy density of the fuel [1-2]. Platinum (Pt) is often used in modern chemistry as an active catalyst in the development of fuel cells [3]. However, it is an expensive metal and easily poisoned by partial oxidation products, such as CO in the methanol oxidation reaction. On the other hand, Titanium dioxide (TiO_2) nanomaterials are excellent photocatalysts and they may serve as a promising electrocatalyst support due to high stability, chemical inertness, low cost, and non-toxicity [4-5].

In this study, TiO_2 nanotube arrays were directly grown on the Ti substrate using anodization. Subsequently, we have modified the fabricated TiO_2 nanotubes using PtIr and PtRu nanoparticles. Scanning electron microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDX) were employed to characterize the fabricated nanostructured electrocatalysts. We further examined the electrocatalytic activity of the PtRu and PtIr nanoparticles deposited on the TiO_2 nanotubes towards the electrochemical oxidation of methanol. Our studies have shown that that PtIr and PtRu nanoparticles with different compositions were successfully deposited on the TiO_2 nanotubes and both exhibited a much higher activity in methanol oxidation than the Pt nanoparticles.

References

[1] M. Tian, G. Wu, A. Chen, *ACS Catal.* 2 (2012) 425-432

[2] P. Waszczuk, J. Solla-Gull, H.-S. Kim, Y. Y. Tong, V. Montiel,*y* A. Aldaz,*y* and A. Wieckowski, *J. Catal.,* 203 (2001) 1

[3] A. Chen, P. Holt-Hindle, Chem. Rev. 110 (2010) 3767-3804

[4] M. Tian, G. Wu, B. Adams, J. Wen, A. Chen, *J. phys. Chem. C.* 112 (2008) 825

[5] SS Thind, G Wu, M Tian, A Chen, *Nanotechnology* 23 (2012) 475706

s7-003

An Electrochemical Impedance Spectroscopy Study of Anion Intercalation in Dual-ion Cells

M. Balabajew, B. Roling
Department of Chemistry, University of Marburg
Hans-Meerwein-Straße, 35032 Marburg/Germany
Marco.Balabajew@chemie.uni-marburg.de

Recently, Placke et al. proposed so called “dual-ion cells” as a new type of energy storage system. In this system, not only the electrolyte cations and the electrodes are involved during the charging and the discharging process but also the electrolyte anions. While charging lithium cations are reduced and deposited at a metallic lithium anode and the electrolyte anions are intercalated in a graphite cathode. By releasing anions and cations back into the electrolyte the battery is discharged (see figure 1). Therefore, the electrolyte (typically based on ionic liquids) does not only act as charge carrier, but also as active material.[1]

Placke et al. reported an extraordinary cycling stability with a capacity retention of more than 99% after 500 cycles. The achievable cell voltage for this kind of cells is about 4.6 V. However, the specific energy is still quite low compared to common lithium-ion batteries.[1]

To further optimize this concept and achieve specific energies comparable to common lithium-ion batteries, it is essential to understand the fundamental processes in this kind of cells. Especially the intercalation of the anion in graphite, which is supposed to be the rate limiting step during charging, is of central interest. Therefore, we used electrochemical impedance spectroscopy to investigate this intercalation process. Measurements were carried out in a 3-electrode setup during the charging and the discharging process in a fully assembled dual-ion cell.

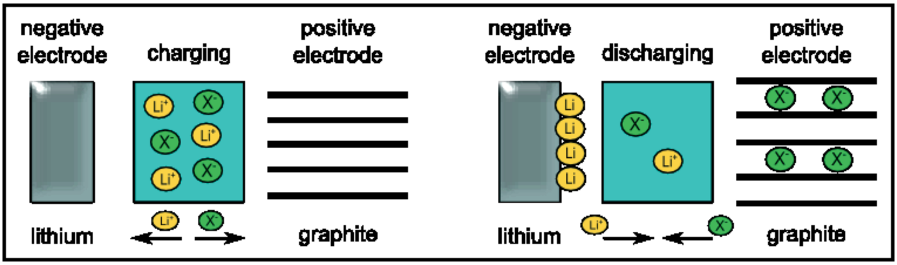


Figure 1: Schematic illustration of a dual-ion cell (adapted from [1]).

[1] T. Placke, P. Bieker, S. F. Lux, O. Fromm, H.-W. Meyer, S. Passerini, M. Winter, Z. Phys. Chem. 226 (2012) 391.

s7-004

Effect of Surface Area on Oxygen Reduction Reaction of Silk-Derived Activated Carbon as PEFC Cathode

H. Fukunaga, J. Fukaya, Y. Hattori, I. Shimada, N. Takahashi, T. Takatsuka
Materials and Chemical Engineering Course, Division of Chemistry and
Materials, Faculty of Textile Science and Technology, Shinshu University
3-15-1 Tokida, Ueda City, Nagano 386-8567 JAPAN
fuku@shinshu-u.ac.jp

Polymer electrolyte fuel cell (PEFC) is expected as one of the key technologies for development of highly efficient energy system. However, platinum, which is used for the electrode catalyst in most PEFCs, is a metal of low abundance and high cost. Therefore, alternative catalyst is required to put PEFCs to practical use. Although many non-precious metal catalysts have been investigated, much of them exhibit low oxygen reduction reaction (ORR) activity or low durability. In recent years, metal oxides and nitrogen containing carbon are reported as novel catalysts, but they are not yet ready for practical use. We have developed silk-derived activated carbon (SAC) as a nitrogen containing carbon catalyst, and used it as a non-precious metal catalyst for the cathode of PEFC[1, 2]. In this study, the effect of surface area of SAC on ORR activity was studied.

SAC was prepared by carbonizing silk fibroin, and was then activated by steam or carbon dioxide. Catalytic activity toward ORR was measured by linear sweep voltammograms (LSV).

ORR activities of SAC, activated by CO_2 for different time, are shown in Fig. 1. LSV measured in O_2-saturated electrolyte solution at 60 °C at 2000 rpm were deducted by those in the deaerated solution. It can be seen that ORR activity increased by activation treatment. SAC activated for 3 h showed the highest ORR activity, and further activation time decreased the activity. The specific ORR current of SAC normalized by mesopore volume was nearly equal at potential above 0.3V, indicating that ORR is dominated by the process in the mesopore.

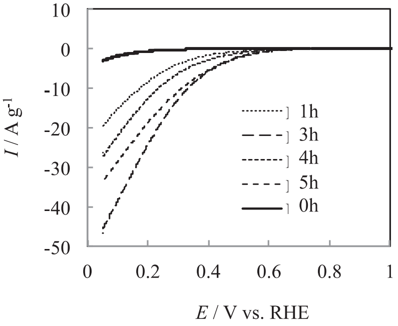


Fig. 1 ORR activity of SAC activated by CO_2 for different time.

s7-005

Effect of Surface Area on Oxygen Reduction Reaction of Silk-Derived Activated Carbon as PEFC Cathode

H. Fukunaga, J. Fukaya, Y. Hattori, I. Shimada, N. Takahashi, T. Takatsuka
Materials and Chemical Engineering Course, Division of Chemistry and
Materials, Faculty of Textile Science and Technology, Shinshu University
3-15-1 Tokida, Ueda City, Nagano 386-8567 JAPAN
fuku@shinshu-u.ac.jp

Polymer electrolyte fuel cell (PEFC) is expected as one of the key technologies for development of highly efficient energy system. However, platinum, which is used for the electrode catalyst in most PEFCs, is a metal of low abundance and high cost. Therefore, alternative catalyst is required to put PEFCs to practical use. Although many non-precious metal catalysts have been investigated, much of them exhibit low oxygen reduction reaction (ORR) activity or low durability. In recent years, metal oxides and nitrogen containing carbon are reported as novel catalysts, but they are not yet ready for practical use. We have developed silk-derived activated carbon (SAC) as a nitrogen containing carbon catalyst, and used it as a non-precious metal catalyst for the cathode of PEFC[1, 2]. In this study, the effect of surface area of SAC on ORR activity was studied.

SAC was prepared by carbonizing silk fibroin, and was then activated by steam or carbon dioxide. Catalytic activity toward ORR was measured by linear sweep voltammograms (LSV).

ORR activities of SAC, activated by CO_2 for different time, are shown in Fig. 1. LSV measured in O_2-saturated electrolyte solution at 60 °C at 2000 rpm were deducted by those in the deaerated solution. It can be seen that ORR activity increased by activation treatment. SAC activated for 3 h showed the highest ORR activity, and further activation time decreased the activity. The specific ORR current of SAC normalized by mesopore volume was nearly equal at potential above 0.3V, indicating that ORR is dominated by the process in the mesopore.

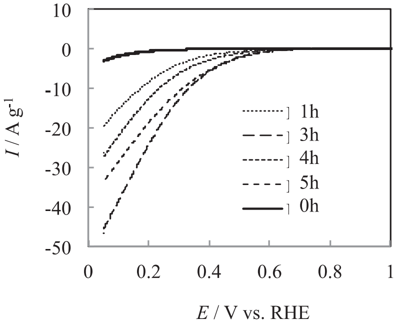


Fig. 1 ORR activity of SAC activated by CO_2 for different time.

s7-006

$LiNi_{0.5}Mn_{1.5}O_4$ Thin-Film Cathodes on Gold-Coated Stainless Steel Substrates: Structural and Electrochemical Properties

M. Gellert, K. I. Gries, J. Zakel, S. Spannenberger, C. Yada, F. Rosciano, K. Volz and B. Roling.
Department of Chemistry, University of Marburg,
Hans-Meerwein-Strasse, D – 35032 Marburg, Germany,
Michael.Gellert@chemie.uni-marburg.de.

Thin films of $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) were prepared on gold-coated stainless steel substrates via a poly(vinylpyrrolidone)-based sol-gel process [1]. Films with different thickness were obtained and characterized in order to achieve a good coulombic efficiency and high capacity. SEI formation on the cathodes was studied by means of electrochemical impedance spectroscopy (EIS), time-of-flight secondary-ion mass-spectrometry (ToF-SIMS) and scanning electron microscopy (SEM). A detailed study of the element distribution at interfaces was done by transmission electron microscopy in combination with energy dispersive X-ray spectroscopy (TEM-EDX) and electron energy loss spectroscopy (TEM-EELS). We have found a mixed oxide interlayer forming at the gold/LMNO interface with approximately 250 nm thickness. In the case of small film thicknesses, the interlayer reduces the capacity and coulombic efficiency of the cathodes drastically. However in thicker films (> 1 µm), the interlayer seems to become electronically conducting and to contribute to the capacity. In this case, a low charge-transfer resistance R_{CT} and a high capacity were observed.

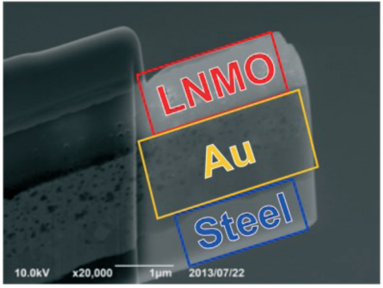


Figure 1: TEM-lammella of an LNMO layer on gold coated steel.

[1] Hoshina K., Yoshima K., Kotobuki M., Kanamura K., *Solid State Ionics* **2012**, *209–210*, 30-35.

s7-007

Effects of metal loading on the structure and activity of Pt-Mn alloys towards ethanol oxidation

Mohammadreza Ghavidel, E. Bradley Easton
Faculty of Science (Chemistry) University of Ontario Institute of Technology
2000 Simcoe St. N., Oshawa, ON CANADA L1H 7K4
mohammadreza.ghavidel@uoit.ca

Increasing catalytic activity while also decreasing the cost associated with Pt-based catalysts is a major research challenge related to direct alcohol fuel cells (DAFC). The wt% of metal deposited on carbon is typically greater than 20% in larger-scale cells in order to achieve high ethanol oxidation performance, thus the loading should be increased from the more often studied 20 wt% on carbon. Unfortunately, increasing the metal loading raises the likelihood of catalyst particle growth and agglomeration, which often results in a reduced electrochemical active surface area (ECSA). Our previous studies have shown that Pt-Mn alloys display high ethanol oxidation reaction (EOR) activity and that heat treatment improves the catalytic properties of the samples. In this research, our main goal was how both the wt% of Pt-Mn deposited and the deposition method impacted the particle dispersion and particle size distribution. Two series of Pt-Mn samples with 20% and 40%wt metal loading has been studied. The electrochemical tests and structural studies showed that by increasing the metal loading, the ECSA value has decrease; as a result, the electrochemical activity has not improved although the Pt loading has doubled. On the other hand, heat treating the samples at 700°C for different periods has no effect on the electrochemical activity of the samples with 40%wt metal loading. However, when sodium citrate is added during the deposition process, the ECSA value was recovered and the activity of the sample with 40%wt metal loadings was greatly enhanced. In addition, heat treatment at 700°C has enhanced the electrochemical activity of the samples to twice that achieved with the untreated samples.

s7-008

Electrochemical Detection of Caspase-3 activity

Vinci Hung, Kagan Kerman*
Dept. of Physical and Environmental Sciences, University of Toronto Scarborough
1265 Military Trail, Toronto, ON, M1C 1A4, Canada
**kagan.kerman@utoronto.ca*

Since the progression of apoptosis follows a strict pathway, the abnormal appearance of specialized apoptotic enzymes, such as cysteine-dependent aspartate-directed proteases (caspases) can be monitored as a biomarker for diseases [1]. In this work, the activity of caspase-3 (C_3) was monitored via electrochemical impedance spectroscopy (EIS). Figure 1 illustrates the design of our label-free electrochemical C_3 assay. Upon incubation in cell lysate of apoptotic cells, the immobilized substrate would be cleaved at the N-terminus. Detection of this interaction was achieved by measuring the changes in charge transfer resistance (R_{CT}) of the electrode surfaces. A decreased value of R_{CT} was attributed to the presence of C_3 in the sample. Verification of C_3 activity in all the samples was also done using a well-established colorimetric optical assay and the results were in agreement. Therefore, the described assay can be successfully utilized in *in vitro* diagnostics and also as a high-throughput technique to test the efficacy of novel C_3 inhibitors as promising anti-cancer agents [2].

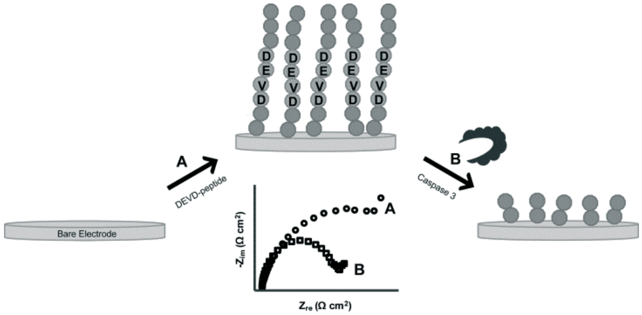


Figure 1. Schematic representation of impedimetric detection technique for C_3 activity. (A) Covalent immobilization of substrate peptide on electrode surface. (B) Cleavage of the substrate peptide by C_3 was detected by electrochemical impedance spectroscopy (EIS).

References: [1] P. J. Barr and L. D. Tomei, Apoptosis and its role in human diseases, Biotechnology 12 (1994) 5.
[2] A.M. Hunter, E.C. LaCasse, R.G. Korneluk, The inhibitors of apoptosis (IAPs) as cancer targets, Apoptosis 12 (2007) 1543.

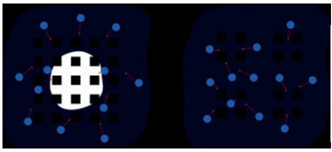
s7-009

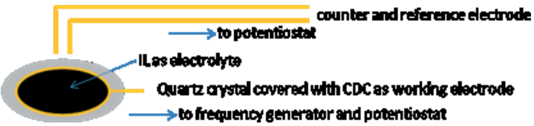
Hierarchically structured Carbide-Derived Carbons and Ionic Liquids as Improved Materials for Supercapacitors?

Thomas Jaensch, B. Roling
Department of Chemistry, University of Marburg
Hans-Meerwein-Straße, 35032 Marburg, Germany
thomas.jaensch[at]staff.uni-marburg.de

For electrochemical energy storage, several types of electrochemical devices are common, among these are Li-ion batteries and electrochemical double layer capacitors (EDLCs). In both cell types, ionic liquids can be used as electrolytes, replacing solutions of salts in organic electrolytes. The non-flammability of ionic liquids and the broad electrochemical window are advantages that outrank their lower conductivity. For EDLCs, the structure and dynamics of the electrode / electrolyte interfacial layers is of considerable interest, as energy storage mainly takes place within the inner-most layers adjacent to the electrodes. [1] The underlying mechanisms of ion transport into the porous material and interactions of ions with functional groups at the surface or ionic interactions in the pores have not been studied exhaustively yet. [2],[3]

In our study, we focus on the interface between an ionic liquid and a hierarchically structured carbide derived carbon. The hierarchical mesoporous structure allows ions to penetrate the porous electrode much faster than in an all-micro porous material. Studies on stored energy in the material are carried out with two complementary methods: electrochemical impedance sprectroscopy and electrochemical quartz crystal microbalance.





[1] P.Simon, Y. Gogotsi, Nat. Mater. 7 (2008), 845. [2] G. Sun et al., Electrochem. Acta 56 (2011), 9248. [3] D. Hulicova-Jurcakova et al., Adv. Funct. Mater. 19 (2009), 1800.

s7-010

Novel Electrochemical Extraction of Lignin from Black Liquor and Its Application for the Removal of Cr(VI)

Wei Jin, Guosheng Wu, Rasha Tolba, Jiali Wen, Aicheng Chen*
Department of Chemistry, Lakehead University
955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada
achen@lakeheadu.ca

Due to the great importance of lignin in environmental and economic consideration, substantial efforts have been made for its extraction from black liquor [1-4]. In this study, we have developed a membrane-assisted electrochemical approach for effective extraction of lignin and recovery of caustic from black liquor. Without addition of acid or CO_2, the pH in the black liquor solution was lowered to 4.7 due to water electrolysis, leading to pH-dependent lignin precipitation and Na^+ ions recovery. Besides, owing to lignin precipitation and oxidation, greater than 70% of the chemical oxygen demand (COD) was removed.
Subsequently, the extracted lignin was employed as the adsorption-release mediator to enhance the electrochemical removal of hexavalent chromium Cr(VI), which is extremely toxic and is classified as human carcinogen, even at trace concentrations. The adsorption and pre-concentration of Cr(VI) was carried out at pH 2.0, while the release and electrochemical reduction was performed at pH 11.0. The 100% efficient release process was due to the complete dissolution of lignin within alkaline solution. The released Cr(VI) ions were electrochemically reduced, forming insoluble $Cr(OH)_3$, which could be easily separated. Based upon the pH-dependent solubility of lignin, this novel electrochemical approach may serve as a promising alternative for the cost-effective extraction of lignin from black liquor and efficient trace Cr(VI) treatment with modulation feasibility.

References:

[1] W. Jin, R. Tolba, J. Wen, K. Li, A. Chen, *Electrochim. Acta* 107(2013), 611-618.

[2] M. Tian, J. Wen, D. MacDonald, R. M. Asmussen, A. Chen, *Electrochem. Commun.* 12 (2010) 527-530.

[3] K. Pan, M. Tian, Z. H. Jiang, B. Kjartanson, A. Chen, *Electrochim. Acta* 60 (2012) 147-153.

[4] R. Tolba, M. Tian, J. Wen, Z.-H. Jiang, A. Chen, *J. Electroanal. Chem.* 649 (2010) 9-15.

s7-011

Extensive Study on the Redox Mechanism of Nickel Hydroxide II; Inhomogeneous Reaction in Nickel Hydroxide Particle

Tetsuro Kobayashi, Yasuhito Kondo, Hidehito Matsuo, Satoshi Yamaguchi,
Hiroshi Nozaski, Takamasa Nonaka and Yoshio Ukyo
Toyota Central R&D Labs., Inc., 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan
tetsuro@mosk.tytlabs.co.jp

Nickel hydroxide $Ni(OH)_2$ is being widely used as a cathode material for Ni-MH and Ni-Cd batteries. Nickel hydroxides have various crystal structures, α-$Ni(OH)_2$, β-$Ni(OH)_2$, β-NiOOH and γ-NiOOH, by their redox reaction. In our previous study, we found new oxidized phase β'-NiOOH (Ni 3.2+) between β-NiOOH (Ni 3+) and γ-NiOOH (Ni 3.7+) and revealed that β'-NiOOH was one of the origin of "Memory effect" as well as γ-NiOOH [1]. "Memory effect" in Ni batteries gives two plateaus in the discharge voltage curve. It is considered that β-NiOOH and β'-NiOOH or γ-NiOOH coexist and that they are reduced independently according to SOC change when "Memory effect" appears. In this study, we have investigated about such an inhomogeneous reaction.

We have developed an in-situ cell with which the redox reaction of a $Ni(OH)_2$ particle in an electrolyte can be observed by using X-rays passing through the cell. The electrode was composed by the single-layer of spherical CoO-coated $Ni(OH)_2$ particles with the diameter of more than 20 μm on a graphite sheet. Figure shows X-ray fluorescence map of Ni in the electrode. XRD and XAFS methods provided us information about changes in crystal structure and Ni valence during the redox reaction. Furthermore, we observed the difference between the change in Ni valence at the center part of a $Ni(OH)_2$ particle and that at the edge part using micro X-ray with the beam size of about 2 μm.

It was found that β-, β'- and γ-NiOOH coexisted in a particle by micro-XRD measurements, and that Ni valence at the edge part of the particle was higher than that at the center part by micro-XAFS measurements, when "Memory effect" appeared. Therefore, it was suggested that β'- and γ-NiOOH, which were the origins of "memory effect", existed around the surface of the particle.

[1] 63rd Annual Meeting of ISE (2012).

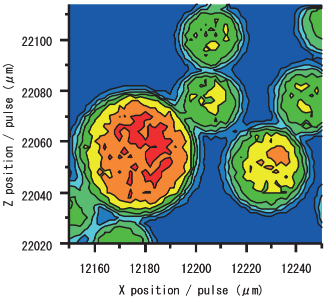


Fig. X-ray fluorescence map of Ni in $Ni(OH)_2$ electrode.

s7-012

Synthesis, Structure and Reactivity of WC@meso-Pt Core-Shell Nano-Electrocatalyst for Fuel Cells

Zhao-Yang Chen,[a] Chun-An Ma,[a,b] You-Qun Chu,[a] Xiao Lin,[b] Jia-Mei Jin,[b]
Christopher Hardacre[b] and Wen-Feng Lin[b]

[a] *State Key Laboratory Breeding Base for Green Chemistry Synthesis Technology, International Sci. & Tech. Cooperation Base of Energy Materials and Application, College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310032, PR China.*
[b] *Centre for the Theory and Application of Catalysis (CenTACat),School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, UK, E-mail: x.lin@qub.ac.uk*

We have developed a facile method to synthesize core-shell WC@meso-Pt nanocatalyst by carburizing ammonium tungstate and copper nitrate via gas-solid reactions, followed by Pt replacement reaction. The mesoporous nanocomposite displays higher activity and stability towards methanol electrooxidation than commercial Pt/C catalyst.

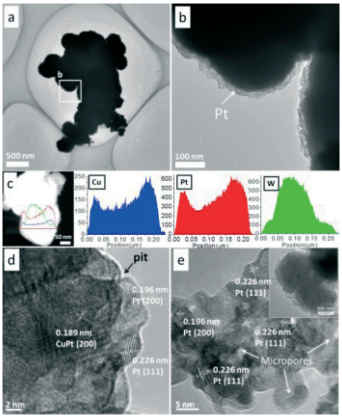


Fig. 1. Transmission electron microscopy (TEM) images (a and b), EDS line-scan analysis (c) and high resolution transmission electron microscopy (HRTEM) image (d) of the as prepared WC@(Cu)Pt sample; and HRTEM image (e) of the WC@meso-Pt sample obtained after the WC@(Cu)Pt being treated by cyclic voltammetry in an acidic methanol solution.

Acknowledgements: This work was supported by the International Science & Technology Cooperation Program of China (2010DFB63680) and the UK EPSRC (EP/I013229/1).

s7-013

The Development and Perspectives of Advanced Batteries

Wenjuan Liu
Microvast Inc.
12603 Southwest Freeway, Stafford, TX, USA 77477
liuwj@microvast.com.cn

Li-ion batteries are one of the most potential candidates as the energy storage devices mainly due to their high energy densities with fairly good rate capabilities and a fairly long cycle life. This technology both drives and is driven by applications, from small sized mobile devices of information technology to large-scale electric vehicles (xEVs) and energy storage systems (ESSs). Many challenges also rise from the effort to increase the specific energy and power, and also to increase the cycle life of the battery. A greater understanding of the Li^+ exchange mechanism will facilitate the development of new active materials with higher performances. This presentation diagnoses the current market trends of LIBs as a primary topic, followed by giving an overview of anode and cathode material candidates of LIBs for xEVs and ESSs based on their electrochemical properties, and also discusses the reactions at the interface of electrode and electrolyte, and the role they play in the successful development of high changing rate (6C, 100% SOC in 10 minutes) and extremely long cyclability (> 20000 cycles) of Li rechargeable batteries in Microvast Inc.

s7-014

Towards functional advanced materials using ordered anodic oxides supports and templates

J.M. Macak*, T. Kohoutek, J. Kolar, T. Wagner
Department of General and Inorganic Chemistry
Faculty of Chemical Technology, University of Pardubice
Nam. Cs. Legii 565, 530 02 Pardubice, Czech Republic
**jan.macak@upce.cz*

Synthesis of highly-ordered nanostructures of valve metal oxides has recently attracted huge scientific and technological interest motivated by their possible use in many applications. The nanoporous Al_2O_3 – most established member of this group of materials – has been prepared by anodic oxidation of Al under suitable electrochemical conditions nearly two decades ago into perfectly ordered, honeycomb-like porous structures. Owing to the flexibility of the pore diameter/length and the relative ease of the Al_2O_3 dissolution, its porous membranes have been since than widely used as templating material of the choice for a range of materials.

It is the TiO_2 that has received the highest attention after Al_2O_3 motivated by its range of applications, including photocatalysis, water splitting, solar cells and biomedical uses. Very significant research efforts have led to reproducible synthesis of self-organized TiO_2 nanotube layers by means of anodic oxidation, during which the starting Ti substrate is converted into highly-ordered nanotubular layer by anodization in suitable electrolyte.

Although many applications of the nanoporous Al_2O_3 and nanotube TiO_2 nanotube layers have been presented, their potential for the synthesis of advanced functional nanomaterials, in particular when considering all possible shapes and geometries, has not at all been exploited.

In the presentation, we want to focus in detail on various filling routes of anodic templates and supports. We will show examples of various functional devices including some very recent results on chalcogenide-sensitized TiO_2 nanotubes [1] and on the new design of resistive switching of memory switching cells using porous AAO templates [2].

1. J.M. Macak, T. Kohoutek, L. Wang, R. Beranek, Nanoscale, 5 (2013) 9541
2. J. Kolar, J. M. Macak, K. Terabe, T. Wagner, J. Mater. Chem. C, 2 (2014) 349.

s7-015

Novel Biosensors for Determination of Phenolic Compounds using Catalyst-Loaded Reduced Graphene Oxide Substrates

Ondrey Kubesa, Samantha Matthews, Kathleen Morrisey, and Maria Hepel*
Department of Chemistry, State University of New York at Potsdam, Potsdam, NY 13676, USA
hepelmr@potsdam.edu

Electrochemical reduction of hydrogen peroxide has been widely applied in designing biosensors based on enzymatic reactions in which H_2O_2 is a common reaction product. The utilization of H_2O_2 detection has enabled achieving high sensitivity of these biosensors and their practical applications, e.g. glucose biosensor based on glucose oxidase enzyme, with H_2O_2 detection have become standard tool for monitoring and maintaining safe glucose level for millions of diabetic patients.

In this work, we have explored further the new ways to enhance the H_2O_2 detection by employing charge transfer mediators and robust distribution and delivery of electrons to the reaction centers based on the excellent properties of graphene monolayer structures [1]. Considerable increase in the cathodic current of H_2O_2 reduction has been achieved using Prussian Blue (PB) modified graphite electrode. Further increase in H_2O_2 catalytic current has been obtained with films of electrochemically reduced graphene oxide (rGO) coated with PB. These sensors have shown excellent catalytic properties for H_2O_2 reduction. However, they were not able to prevent the interfering oxidation of ascorbic acid which is prevalent in biological samples. To resolve the problem of interfering species, the application of interferent screening has been attempted. We have found that using a sensor for H_2O_2 with interferent screen COPO, it is possible to detect H_2O_2 in the concentration range from 10 to 500 μM in the presence of a large excess of ascorbic acid (1 mM).

In further studies, we have designed enzymatic biosensors based on horse radish peroxidase and laccase for the detection of catechol as a representative of polyphenolic compounds.

In summary, we have designed and tested a new type of substrates for enzymatic biosensors. We have found that the rGO/PB electrodes can serve as an excellent basis for these biosensors, showing high sensitivity and durability, and with addition of interferent screening, high selectivity without any loss of sensitivity.

References

1. A. K. Geim, K. S. Novoselov, *Nat. Mater*. 6 (2007) 183-191.

s7-016

Sensitive Detection of Hemoglobin with Electrodes Modified with Magnetic Nanoparticles

Edyta Matysiak, Anna M. Nowicka
University of Warsaw, Faculty of Chemistry
Pasteura 1, 02-093 Warsaw, Poland
e-mail address: ematysiak@chem.uw.edu.pl

Application of magnetic nanoparticles and an external magnetic field gave a possibility of enhanced transport of oxygen molecules and iron complexes to the electrode surface. This effect must lead to an increase of the analytical signal. Next we turned to hemoglobin. Hemoglobin plays a very important role in the living organisms. This molecule is an oxygen carrier in the human body. Also, hemoglobin is a blood protein which contains iron. Iron(III) in hemoglobin is a paramagnetic species.

Here we present a simple biosensor for hemoglobin detection. In the first step the electrode was modified with magnetic nanoparticles (Fe@C and Fe_3O_4). The presence of nanomagnets at the electrode surface and application of external magnetic field allowed us to increase substantially the hemoglobin flux to the electrode surface. The analytical reduction signal was obtained using cyclic voltammetry and differential pulse voltammetry. The obtained detection limit was circa 0.2 nM. Additionally the stability and reproducibility of the signal was very good.

s7-017

Effect of Nanoscale Catalyst Structure on the Mass Transport Properties in Cathode Catalyst Layers of PEM Fuel Cells

A. Nouri-Khorasani, D.P. Wilkinson
Department of Chemical and Biological Engineering, The University of British Columbia
2360 E Mall, Vancouver, BC, V6T 1Z3, Canada
anouri@chbe.ubc.ca

Lowering the precious metal loading while maintaining or improving performance is one of the key areas of focus for fuel cells research. Engineered catalyst layers with nanostructured Pt-based structures can outperform conventional Pt/C catalyst layers in PEM fuel cells at lower Pt loadings, due to higher intrinsic catalytic activity and durability, as well as enhanced mass transport conditions.

An interconnected network of Pt nanowires is a suitable candidate for the cathode catalyst layer (CCL) in PEM fuel cells, due to its high surface area and low Pt loading. It also offers the possibility to engineer the catalyst layer, since its nanostructure can be easily modified using such techniques as templated electroless deposition.

In this work, we present a model to characterize the effect of nano-to-meso-scale nanowire catalyst geometry on the mass transport and activity in the CCL. We modeled the Pt nanowires templated on the Nafion membrane as a network of interconnected cylindrical wires on an electrically insulating substrate.

In this model, we investigated the effects of surface and subsurface Pt structures, nanowire radius and length, as well as network interconnectivity, on the performance of the CCL. Assuming independent kinetics and mass transport phenomena for the CCL, the enhancement in catalytic performance can be associated with enhanced mass transport conditions in the catalyst layer.

s7-018

Aggregation of Trichogin in a Lipid Monolayer Deposited at the Au(111) Electrode surface

Maxim Smetanin[1], Flavio Maran[2], Jacek Lipkowski[1]
1.Department of Chemistry, University of Guelph, Guelph, ON, Canada N1G 2W1
2. Department of Chemistry, University of Padova, Via Marzolo 1, 35131, Padova, Italy
smetanin@uoguelph.ca

Trichogin is a short antimicrobial peptides (AMP) consisting of ten amino acid residues. It belongs to the family of naturally occurring peptaibols with antibiotic properties. The single trichogin molecule is much shorter than membrane thickness. However fluorescent experiments have shown that the peptide is capable to induce membrane leakage. To extend our understanding of the mechanism of trichogin action on biological membranes we studied a mixed film of trichogin and phospholipid molecules formed at the electrode surface by Langmuir-Blodgett technique. The structure of the pore formed by trichogin molecules in a monolayer of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) was studied by electrochemical scanning tunneling microscopy (EC-STM). It was observed that trichogin molecules form well-ordered 2D nanocrystals within the DMPC monolayer. The pores have hexagonal structure and consist of six peptide molecules.

s7-019

Free-Standing Paper-Based Nano-Carbon Composites as Binder-Free Anode for Lithium Ion Batteries

Biqiong Wang[1,2], Yuhai Hu[1], Xifei Li[1], Jian Liu[1], Biwei Xiao[1], Mohammad Banis[1],
Ruying Li[1], Mei Cai[3], Tsunkong Sham[*,2], Andy X. Sun[*,1]
1. Department of Mechanical and Materials Engineering, University of Western Ontario
2. Department of Chemistry, University of Western Ontario
London, Ontario N6A 5B8, Canada
3. General Motors R&D Center, Warren, 48090-9055, MI, USA
bwang252@uwo.ca

Free-standing flexible electrodes are highly demanded in lithium ion battery (LIB) [1]. Among various anode materials for LIBs, $Li_4Ti_5O_{12}$ (LTO) has been intensively investigated for its excellent cycling performance and reversibility in the charge-discharge process as well as structure stability and thermal stability. [2] However, a limiting factor for a wider application is its poor conductivity. An effective way is to introduce some highly conductive materials to synthesize composites. Graphene is ideally suited not only for its exceptional conductivity but also for a novel macrostructure, free-standing papers, built up due to its outstanding mechanical properties. [3] Apart from the flexibility of the papers, the fabrication of LIBs can be simplified without using binders and current collector (Cu foil) so that the weight of the batteries is effectively reduced.

Herein, we presented a composite of graphene[4], graphene-CNTs[5], graphene-Si nanowires, graphene-MoS_2[6], and graphene-LTO paper sheets by vacuum-assisted filtration. Taking LTO as an example, the as-prepared LTO was synthesized using hydrothermal method. [2] The initial amount of LTO added into the system was varied and a non-linear dependence of the specific capacity on it was observed. With an initial amount of 10mg LTO, the discharge capacity remained 164.8 $mAhg^{-1}$ after 50 cycles tested at a rate of 100 mAg^{-1} while those of the initial amount of 0, 20, and 30 mg dropped below 140 $mAhg^{-1}$.

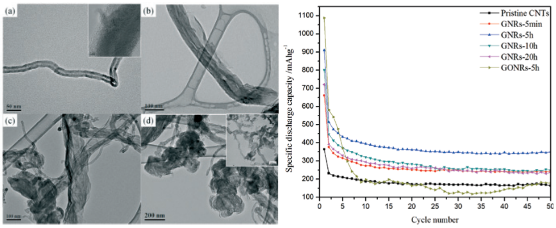
[1] H. Gwon, J. Hong, H. Kim, D.H. Seo, S. Jeonb, and K. Kang, ***Energy Environ. Sci.***, 2014, DOI: 10.1039/c3ee42927j
[2] J. Chen, L. Yang, S. Fang, Y. Tang, ***Electrochimica Acta***, 55 (2010) 6596–6600
[3] G. Zhou, F. Li and H. H. Cheng, ***Energy Environ. Sci.***, 2013, DOI: 10.1039/C3EE43182G
[4] Y. Hu, X. Li, D. Geng, M. Cai, R. Li, X. Sun, ***Electrochim. Acta*** 91 (2013) 227-233
[5] Y. Hu, X. Li, J. Wang, R. Li, X. Sun, ***J. Power Sources*** 237 (2013) 41-46
[6] Y. Hu, X. Li, A. Lushington, M. Cai, D. Geng, M. Banis, R. Li, X. Sun, ***ECS J. Solid State Sci. Technol.*** 2 (2013) M3034-M3039

s7-020

Graphene Nanoribbons Derived from the Unzipping of Carbon Nanotubes: Controlled Synthesis and Superior Lithium Storage Performance

Biwei Xiao, Xifei Li, Xia Li, Biqiong Wang, Craig Langford, Ruying Li, Andy X. Sun*
Department of Mechanical and Materials Engineering, University of Western Ontario, London, ON, Canada N6A 5B9
(* corresponding author; email: xsun9@uwo.ca)

Graphene nanoribbons (GNRs) from chemical unzipping of carbon nanotubes (CNTs) have been reported to be a suitable candidate for lithium ion battery materials, but very few of them focused on controlling GNRs with different unzipping levels.[1-3] Here we present a study of GNRs with controlled unzipping level and the prevailing factors that affect the lithium storage performance at early and final unzipping level, along with the effect of thermal reduction. Based on Raman and BET surface area tests, we found that the unzipping of CNTs starts with surface etching, then proceeds to partial and full unzipping, finally fragmentation and aggregation. Galvanostatic charge-discharge reveals that the defect increase is mainly responsible for the capacity enhancement at the early unzipping level, while surface area drop is associated with the capacity fade at final unzipping level. The surface functional groups can result in low electrical conductivity and, therefore, causes capacity drop within several cycles. The GNRs with controlled unzipping level display different electrochemical behaviors, thus can provide rational choices for researchers who are searching for desired functions using GNRs as additives in lithium ion batteries.[4]



TEM images of GNRs at different unzipping stage and discharge capacity

References:

[1] M. Terrones, A.R. Botello-Méndez, J.-C. Charlier et al., *Nano Today*, **5** (2010) 351-372.

[2] T. Bhardwaj, A. Antic, B.D. Fahlman et al., *J. Am. Chem. Soc.*, **132** (2010) 12556-12558.

[3] A.L.H. Dmitry, V. Kosynkin, J. M. Tour et al., *Nature*, **458** (2009) 872-876.

[4] B. Xiao, X. Li, X. Sun et al., *J. Phys. Chem. C*, revised

s7-021

Nanostructured Carbon Based Electrode Materials for Rechargeable Li- and Na-Air Batteries

Hossein Yadegari, Yongliang Li, Ruying Li, Xueliang Sun
Department of Mechanical and Materials Engineering, University of Western Ontario
London, Ontario N6A 5B9, Canada
xsun@eng.uwo.ca

Rechargeable metal-air batteries are widely considered as the next generation high energy density electrochemical storage devices. The performance and rechargeability of these metal-air cells is highly dependent on the positive electrode material, where oxygen reduction and evolution reactions take place. Nitrogen doped carbon nanotubes (N-CNT) [1], graphene nanosheets (GNS) [2], nitrogen-doped graphene nanosheets (N-GNS) [3, 4], sulfur doped graphene nanosheets (S-GNS) [5] and heat-treated carbon black materials [6] were synthesized and applied as gas diffusion electrodes of Li- and Na-air cells. For example, N-GNS electrode material demonstrated superior discharge capacity of 11660 and 8600 mA g^{-1} in Li- and Na-air cells, respectively, at a current density of 75 mA g^{-1}. The enhanced performance of N-GNSs is attributed to the active sites introduced by nitrogen doping process. Further, discharge capacity of heat-treated carbon black materials is shown to be linearly correlated with specific surface area of the electrode materials. In addition, direct electron microscopic observations revealed that discharge product's morphology of Li- and Na-air cells are greatly influenced by positive electrode materials. Furthermore, chemical composition of discharge product as well as charging overpotential of the Na-air cell is illustrated to be managed by manipulating the discharge reaction kinetics (Figure 1).

[1] Y. Li. X. Sun, et al., *Electrochem. Commun.*, **2011**, 13, 668-672.
[2] Y. Li. X. Sun, et al., *Chem. Commun.*, **2011**, 47, 9438-9440.
[3] Y. Li. X. Sun, et al., *Electrochem. Commun.*, **2012**, 18, 12-15.
[4] Y. Li. X. Sun, et al., *Chem. Commun.*, **2013**, 49, 11731-11733.
[5] Y. Li. X. Sun, et al., *J. Mater. Chem.*, **2012**, 22, 20170-20174.
[6] Y. Li. X. Sun, et al., *Carbon*, **2013**, 64, 170-177.

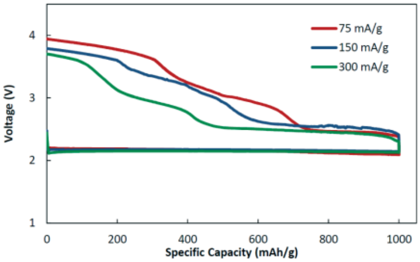


Figure 1: Limited discharge and charge curves of Na-air cells using heat-treated carbon material at different discharge current densities of 75, 150 and 300 mA g^{-1} and a constant charge current density of 40 mA g^{-1}.

s7-022

The continuous treatment of trivalent and hexavalent chromium wastewater using electrodeionization as a new approach

Zhaoyang Zhang, Daniel Liba, Aicheng Chen
Department of Chemistry, Lakehead University,
955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada
zzhang9@lakeheadu.ca, achen@lakeheadu.ca

Chromium is of environmental, health, and industrial importance, found naturally in soils, rocks, plants and animals, but also waste is produced excessively from various industries such as stainless-steel production, leather tanning, paint and pigment fabrication [1-3]. Hexavalent chromium (Cr(VI)) are very toxic, and have been classified as a carcinogenic agent in humans by the IARC (International Agency for Research of Cancer). Both oxidation states of chromium are often found together from industry or oxidizing or reducing agents found in nature and it is therefore very important to develop methods to adhere to treat both Cr (VI) and Cr (III) [4]. In the present work, continuous ion exchange and electrodeionization are proposed as a new hybrid technology for the effective treatment of Cr(VI) and Cr(III) wastewater as well as the recovery of chromium ions.

In this study, a strong basic macroreticular anion exchange resin (Amberlite® IRA900) has been systemically investigated for the removal of Cr(VI) and Cr (III). A method of measuring the concentrations of Cr (III) and Cr (VI) within the same solution was developed by employing the combination of both UV-Vis spectroscopy to measure the concentration of Cr (VI) and ICP-AES to measure the total concentration of chromium where the difference was the concentration of Cr (III). The limiting current of the Cr (VI) setup was successfully determined to be 15 mA by measuring the current-voltage relationship with the use of a potentiostat. When the anionic resin was combined with a strong acidic macroreticular cation exchange resin (Amberlite® 200C) and employed in continuous electrodeionization, over 92.7% of Cr(VI) and 94.8% of Cr(III) was continuously removed from the dilute compartment, while Cr(VI) and Cr(III) was recovered in the concentrate compartment. The saturation effect of resins were also investigated starting initially with unsaturated ion exchange resins and it was found that the electrodeionization process had very effective removal rate of Cr(VI) in the range of 90 to 97% after 17th treatments. It was also found that as more treatments were done, the energy consumption decreased indicating enhancement of conductivity in the resin bed.

References

[1] Mihçiokur, H.; Peker I.; D*esalination and Water Treatment* **2013**, 51, 2116–2120

Index